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THEORY OF THE END-POINT IN ELECTROMETRIC TITRATION

BY P. S. ROLLER

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In a paper recently published by Eastman[1] on the theory of the electrometric titration of an acid by a base, certain conclusions among others were drawn to the effect that the inflection point in the e.m.f. titration curve would not appear when the ionization constant of the acid of a given concentration is below a certain magnitude, in particular that it would not appear when $K_A \leqq 10^{-12}$ for a 1.0 molar acid, or when $K_A \leqq 10^{-9}$ for a 0.001 molar acid. In attempting to confirm this result, we have been able to generalize the theory of the end-point in electrometric titration, and in a subsequent paper consider by the method of analysis here used the electrometric (and colorimetric) titration of polybasic acids, weak base salts, and their mixtures, by a base or mixture of bases.

We also find here that there is a discrepancy between our result for the appearance of the inflection point and that of Eastman. We may without sensible error consider the exact equation (10a) below as of the third degree and, testing for real roots, we find that the condition of the appearance of an inflection point in the titration of a weak acid by a strong base is that $cK_A > 27K_w$, where K_A is the ionization constant of the acid, K_w the ion product constant of water and c is a concentration defined by the following equation:

$$\frac{1}{c} = \frac{1}{a} + \frac{1}{b} \tag{1}$$

where a is the initial concentration of the acid and b is the initial concentration of the base in the titrating solution. We have checked this condition numerically. We see then that an inflection point should appear when K_A is as low as 3×10^{-13} for a 1 normal acid, neglecting dilution. The discrepancy between this result and that of Eastman appears to be **due** to an oversight in his numerical calculation of an otherwise correctly derived equation.

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[1] Eastman, THIS JOURNAL, **47**, 332 (1925).

Determination of the H-Ion Concentration at the End-Point and at the Inflection Point

In a plot of E, the e.m.f. of the H_2 half cell, against n/n_e, the fraction of the number of cc.'s required to reach the end-point, the condition for an inflection point is, from the equation

$$E = 0.059 \log x = -0.059\, px \tag{2}$$

that

$$\frac{d^2n}{dx^2} = -\frac{1}{x}\frac{dn}{dx} \tag{3}$$

where x is the H-ion concentration in the solution, px is the PH of the solution and n is the number of cc. of titer.

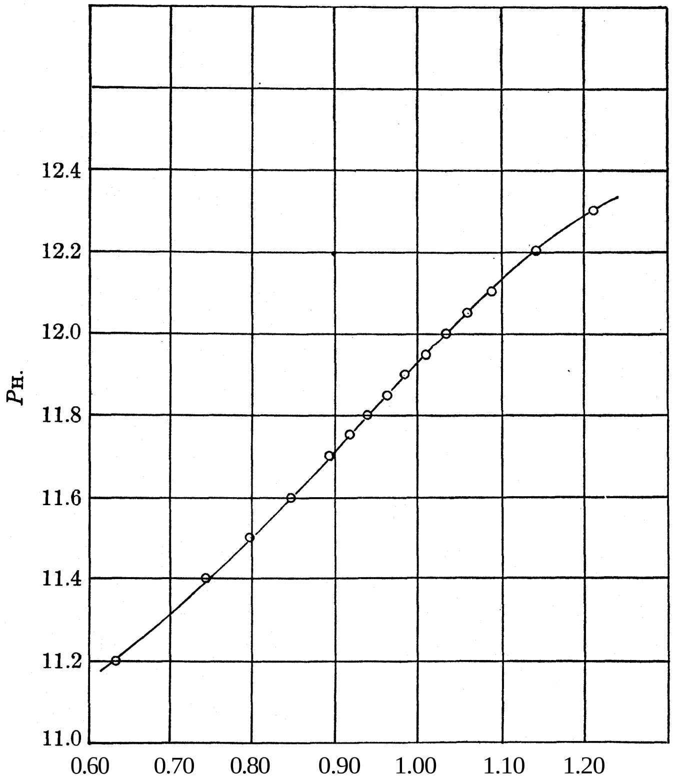

Fig. 1.—P_H *vs.* fraction titrated, n/n_e. $K_A = 10^{-11}$, $a = 0.1$, $b = 0.4$.

We can obtain an exact relation between n and x as follows. Let b represent the concentration of the base in moles per liter, v the initial volume of the solution, x the concentration of the non-ionized part of the acid HA of initial concentration a, and y the OH^- concentration in solution. In an infinitesimal addition of titrating solution the number of moles of

OH-ion added per unit volume is $[b/(V+n)]\mathrm{d}n$. This quantity is divided in the solution between increasing the OH--ion concentration, and decreasing the H^+ and HA concentrations. The following equation accounts for the distribution within the solution of the added OH^- ion, allowing for dilution of the solution by the added titer

$$\frac{b}{V+n}\,\mathrm{d}n = \mathrm{d}y - \mathrm{d}x - \mathrm{d}z + \frac{(y-x-z)}{V+n}\,\mathrm{d}n \tag{4}$$

This equation may be simply integrated if we take as the variables b and $(y - x - z)$. The integration constant is determined by the condition that, when $n = 0$, $(a - z) + y = x$, which expresses the electrical neutrality of the solution, so that upon integration of (4) we obtain

$$\frac{bn}{V} = a + \left(1 + \frac{n}{V}\right)(y - x - z) \tag{5}$$

n in (5) may be obtained as a function of x alone by eliminating y and z by means of the following ionization equations

$$xy = K_w \tag{6}$$

$$\frac{x\left(a\,\frac{V}{V+n} - z\right)}{z} = K_A \tag{7}$$

In (7), the ionization equation of the acid, we have assumed that the salt formed is 100% ionized. If it is not, a simple correction must be made to K_A for the degree of dissociation; or an activity coefficient correction may be applied to both K_A and K_w.

At the end-point we have by definition that

$$\frac{bn_e}{V} = a \tag{8}$$

We have then upon substituting from (6), (7) and (8) in (5) an equation in x_e, the H-ion concentration at the end-point

$$\left(1 + \frac{a}{b}\right)\left(\frac{K_w}{x_e} - x_e\right) - \frac{ax_e}{(K_A + x_e)} = 0 \tag{9a}$$

This is a third-degree equation in x_e, but from the physical nature of the problem two of these roots must be imaginary. Expanding $1/(K_A+x_e)$ in powers of x_e/K_A, we finally obtain, in the titration of a weak acid, that

$$x_e = \sqrt{\frac{K_w K_A}{c}}\left[1 + \frac{1}{2}\sqrt{\frac{K_w}{cK_A}} - \frac{1}{8}\,\frac{K_w}{cK_A}\cdots\right] \tag{9}$$

where c is a concentration defined by Equation (1).

This equation for the H-ion concentration at the end-point is practically identical with the usual result obtained in the calculation of the hydrolysis of a normal salt. The effect of dilution by the added titer is contained by virtue of c in the term $1/b$, the reciprocal of the concentration of the base in the titrating solution, which may usually be neglected, against $1/a$, the reciprocal of the initial concentration of the acid in the solution. In that event, we may replace c by a in (9).

We must now determine x_i, the H-ion concentration at the inflection point. Differentiating (4), (6) and (7) with respect to x and substituting in (2) we finally obtain

$$2\left(1+\frac{a}{b}\right)\frac{K_w}{x_i^3}+\frac{2aK_A}{(K_A+x_i)^3}=\left(1+\frac{a}{b}\right)\frac{K_w}{x_i^3}+\frac{aK_A}{x_i(K_A+x_i)^2}+\left(1+\frac{a}{b}\right)\frac{1}{x_i} \tag{10a}$$

This fifth-degree equation has at least one real root. We are interested in the root in the neighborhood of the end-point. Expanding then in a binomial series in powers of x_i/K_A we find for the H-ion concentration at the inflection point

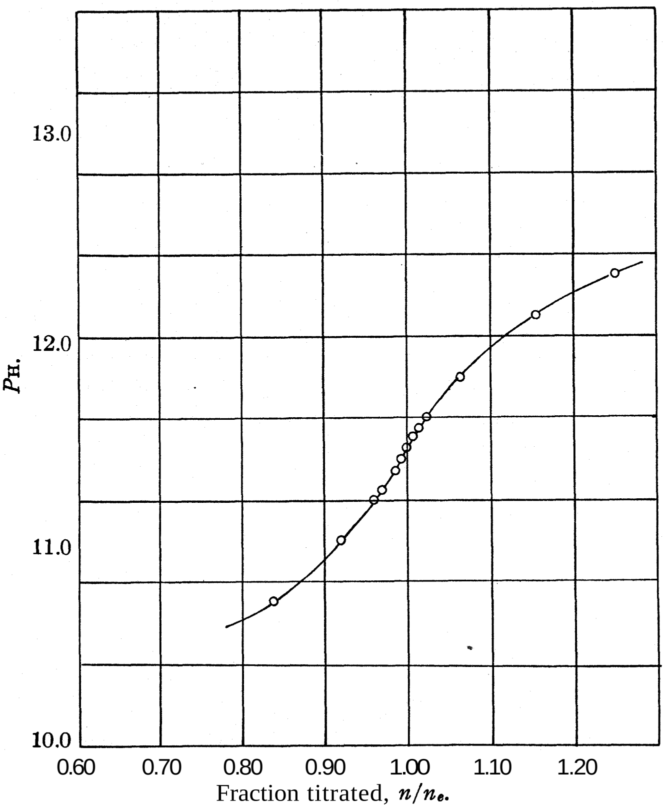

Fig. 2.—PH *vs.* fraction titrated, n/n_e. $K_A = 10^{-10}$, a = 0.1, b = 0.4.

$$x_i = \sqrt{\frac{K_wK_A}{c}}\left[1+2\sqrt{\frac{K_w}{cK_A}}+\frac{3}{2}\frac{K_w}{cK_A}+\ldots.\right] \tag{10}$$

From this approximation equation for a weak acid, which holds very closely for K_w/cK_A as large as 10^{-2}, we see that the H-ion concentration at the inflection point is finite and real, at least for all values such that the series is convergent, that is, for $cK_A > K_w$. However, from the exact equation (10a), the condition is $cK_A > 27K_w$. Since $x_i > x_e$ the inflection point always precedes the end-point, except when the acid is strong ($K_A \longrightarrow \infty$). In that case $x_i = x_e = \sqrt{K_w}$, a result obtained from (9a) and (10a).

We have for the difference in *PH* between the end-point and the inflection point from (9) and (10)

$$Px_e - Px_i = 0.65\sqrt{\frac{K_w}{cK_A}} \tag{11}$$

Thus from this equation the difference in *PH* between the end-point and the inflection point, which is seen to be very small, depends not only upon K_A but also, and in the same way, upon the acid and base concentration, that is, upon the product cK_A, where $1/c = 1/a + 1/b$ by (1), and increases as cK_A decreases.

This difference in *PH* may be obtained in terms of the difference in cc. of titer between the inflection point and end-point by means of the general relation

$$\frac{\Delta n}{n_e} = \left(\frac{\mathrm{d}n}{\mathrm{d}x}\right)_{x_e < x < x_i} \Delta x \tag{12}$$

$\Delta n/n_e$ represents the deviation of the end-point from the inflection point as a fraction of the total titer required to reach the end-point, Δx being equal to $x_i - x_e$, and An to $n_i - n_e$.

We thus obtain for the fractional deviation, $\Delta n/n_e$, upon calculation by means of this equation

$$\frac{\Delta n}{n_e} = -\frac{3K_w}{cK_A} \tag{13}$$

TABLE I

RESULTS OF CALCULATIONS

cK_A	$Px_e - Px_i$	Px_e ($c = 1.10$)	$100\frac{Px_e - Pxi}{Px_e}$	$-100\frac{Am}{n_e}$
10^{-8}	0.00065	10.0	0.01	0.0003
10^{-10}	.0065	11.0	.06	.03
10^{-11}	.0206	11.50	.18	.30
10^{-12}	.065	12.00	.54	3.0

In Table I above, we have made numerical calculations of the deviation of the end-point from the inflection point for a series of acids. In Col. 1 is given the product cK_A ranging from 10^{-8} to 10^{-12}. In the second column is given corresponding to each product cK_A the difference in PH between the inflection and end-points calculated from (11) with $Kw = 10^{-14}$, in the third column is the *PH* at the end-point for $c = 0.10$ calculated from (9), in the fourth column is the percentage deviation in *PH* between the end-point and the inflection point and in the last column is given the percentage titer deviation calculated from (13).

From this table it is seen that when the product of the concentration into the ionization constant is equal to 10^{-11} the titer deviation of the end-point from the inflection point is 0.3%, but only 0.03% when the product is equal to 10^{-10}, decreasing rapidly thereafter. For $cK_A = 10^{-12}$, the deviation is 3.0%. Inasmuch as when the product cK_A is as small as 10^{-12} the error of titration, if it can be performed at all, is of a greater magnitude than the last result would indicate, we must look for a different cause of the increased error. The answer seems to lie in the physical difficulty of locating the inflection point, in a plot of E against n/n_e, when the product of the concentration into the ionization constant becomes so small. This, of course, is a matter apart from the error due to the difference, $px_e - px_i$.

The Error of Locating the Inflection Point

In the neighborhood of the inflection point the curve is symmetric about a horizontal axis passing through it. Consider the points P and P' in the neighborhood of the inflection point symmetrically located with respect to it. If the tangent to all three points is the same, it is clear that it will be impossible to distinguish the inflection point lying between P and P', since then the curve degenerates into a straight line.

This leads us to suspect that it is the difference in slope at P (or P') and at the inflection point that determines the error of locating the latter on the curve. We distinguish the inflection point from other points by the fact that at that point the slope of the curve is a maximum and therefore is the more readily differentiated as its slope is greater than that of other points in its neighborhood. This may perhaps be more readily seen when we consider a plot[2] of $\Delta E/\Delta\left(\frac{n}{n_e}\right)$ against n/n_e, in which case the ordinates are proportional to the slope of the usual titration curve while the inflection point is now a maximum point. This maximum is the more accurately located the steeper the curve.

We have for the slope of the tangent to the curve at any point by differentiating (2)

$$\frac{\mathrm{d}E}{\mathrm{d}\left(\frac{n}{n_e}\right)} = -\frac{0.059}{2.302}\,\frac{1}{\left[\frac{K_w}{cx} + \frac{x}{a} + \frac{}{(K_A + x)^2}\right]} \tag{14}$$

At the inflection point, substituting for x_i from (10), we have

$$\left[\frac{\mathrm{d}E}{\mathrm{d}\left(\frac{n}{n_e}\right)}\right]_{x_i} = \frac{0.059}{4.604}\sqrt{\frac{cK_A}{K_w}} \tag{15}$$

Let us choose our arbitrary reference point P at the 91% neutralization point. We have by (7) for the H-ion concentration at P, $x_P = 0.1K_A$.

Upon substitution in (14) we obtain for the slope at the point of reference, P

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[2] Cox, This Journal, 47, 2138 (1925).

$$\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{xP} = -\frac{0.059}{2.302}\,\frac{1}{\left(\frac{10K_w}{cK_A} + 0.0825\right)} \qquad (16)$$

Thus the difference in slope at P and at the inflection point depends by equations (15) and (16) only upon the product, cK_A, with $1/c = 1/a + 1/b$, similarly to previous results.

Table II

Calculated Differences

cK_A	$\frac{1}{0.059}\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{x_i}$	$\frac{1}{0.059}\left[\frac{dE}{d\left(\frac{n}{n_e}\right)}\right]_{xP}$	Difference
10^{-6}	2160	5.2	2155
10^{-8}	216	5.2	211
10^{-10}	21.6	5.2	16.4
10^{-11}	6.9	4.6	2.3
10^{-12}	2.4	2.4	0.0

In Table II we have calculated the differences in a plot of $E/0.059 (= P_H)$ against n/n_e between the slope at the 91% neutralization point and at the inflection point for cK_A from 10^{-6} to 10^{-12}. The first column gives the magnitude of the product cK_A, the second gives the slope at the inflection point, the third gives its value at the 91% neutralization point, the fourth shows the difference in slope at these two points.

It is seen that the difference falls off rapidly as we go from cK_A equal to 10^{-6} to cK_A equal to 10^{-11}. At cK_A equal to 10^{-12}, the slopes are practically equal, so that the whole curve in the vicinity of the inflection point tends to contract into a straight line. However, in spite of this, the inflection point may still be located even for $cK_A = 10^{-12}$, though here the error may be considerable in the usual plot of E against n/n_e, where, in order to observe that there is any inflection in the curve at all, it must be plotted over a large range in n/n_e, say from 0.65 to 1.25.

Graphical Illustration

In the titration of a weak monobasic acid by a strong base, we have plotted P_H against n/n_e from Equation (5) for the two acids $K_A = 10^{-10}$, $K_A = 10^{-11}$, each of initial molar concentration a = 0.10, and with b, the strength of the titrating solution, equal to 0.4.

Examination of these curves shows the following.

1. There is an inflection point in both cases. It is visible for $K_A = 10^{-11}$ only upon close scrutiny of the curve as a whole, but it may not be sharply located. The error of locating it will by comparison of the curves obviously be much less for the stronger acid, $K_A = 10^{-10}$.
2. Ascertaining the position of the inflection point as best we may, the difference in P_H at the end-point where $n/n_e = 1.0$ and at the in-

flection point appears to be $+0.09 \pm 0.06$ for $K_A = 10^{-11}$ and $+0.02 \pm 0.02$ for $K_A = 10^{-10}$. By Equation (11) we would calculate these PH differences to be $+0.073$ and \$0.023, respectively.

Corresponding to the above PH differences, we have again from the curves for the deviations in cc. of titer for $K_A = 10^{-11}$ $4 \pm 4\%$, for $K_A = 10^{-10}$ $0.3 \pm 0.3\%$. By Equation (13) we calculate these titer deviations to be 3.7 and 0.37%, respectively. While the calculated PH and titer differences agree well with the observed, there is an error in the observed values which is due to the uncertainty of locating the inflection point on the curve. The magnitude of this error is closely equal to the differences themselves.

The graphs here considered represent an ideal case in that there are no errors of reading the e.m.f., buret, etc., and the number of points taken is greater. Consequently in any experimental plot of e.m.f. against n/n_e, the error of locating the inflection point will doubtless be greater than is indicated by the above results.

The writer wishes to record his appreciation of the helpful advice rendered by Professor H. A. Fales of this University.

Summary

1. In the electrometric titration of a monobasic acid by a strong base, an inflection point in the e.m.f. titration curve will appear if $cK_A < 27K_w$.
2. Simple equations are deduced for the difference in PH and in cc. of titer between the inflection point and the end-point. The former always precedes the latter. The differences which are usually negligible increase with the weakness of the acid and with the dilution.
3. Apart from these calculable differences, there is an error of locating the inflection point. This error arises from the tendency of the curve to compress into a straight line in the neighborhood of the inflection point as the acid is weaker or the dilution greater.

NEW YORK, N. Y.

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

THE CUPROUS CHLORIDE ELECTRODES

BY RALPH F. NIELSEN[1] AND DENTON J. BROWN

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The Copper Amalgam–Cuprous Chloride Electrode

Introduction

The copper-cuprous chloride electrode has been measured by Immerwahr,[2] by Luther and Wilson,[3] and by Noyes and Chow.[4] These investigations are subject to the errors of not using a reproducible form of copper, of not preparing the electrodes in the absence of oxygen and of not rotating the electrodes to insure equilibrium. Luther and Wilson employed the cell Cu, CuCl(s), KCl(N/20), N. E. Noyes and Chow employed the cell Cu, CuCl(s), HCl, H_2. Immerwahr used the cell Cu, CuCl(s), KNO_3(N) + HCl(N/20), N. E., in which the complete cell reaction is obviously doubtful.

In our work we first used the cell Cu(amalgam), CuCl, HCl, HgCl, Hg, since it has the advantage of having an electromotive force practically independent of concentration. We tried to follow the method of Ellis[5] in preparing the calomel electrodes, since he obtained results which varied only a few hundredths of a millivolt. This was essentially the electrolytic method of Hulett.[6] We were, however, unable to obtain constant values, and when we rotated the calomel electrodes for a day or two, as he recommends, we obtained values which were nearly ten millivolts too high, as indicated by comparison with hydrogen electrodes. The same results were obtained with a second preparation of electrolytic calomel. For this reason we employed the cell Cu(amalgam), CuCl(s), HCl, H_2.

Apparatus and Solutions

The copper amalgam was the same two-phase electrolytic amalgam as that described in our previous paper on the potential of copper.[7] Cuprous chloride was prepared directly in the electrode vessel by addition of a solution of chloro-cuprous acid to water, while a stream of purified nitrogen bubbled through the vessel. The chlorocuprous acid was prepared by reduction of a hydrochloric acid solution of cupric chloride

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[1] This paper is taken from part of a thesis submitted by Ralph F. Nielsen for the degree of Doctor of Philosophy at the University of Nebraska. The problem of the determination of the free energies of copper compounds was selected by him at the suggestion of Professor Merle Randall of the University of California and this paper represents the work on the copper chlorides.

[2] Immerwahr, Z. *Electrochem.*, 7, 477 (1900).

[3] Luther and Wilson, *Z. physik. Chem.*, 34, 488 (1900).

[4] Noyes and Chow, THIS JOURNAL, 40, 739 (1918).

[5] Ellis, ibid., **38,** 737 (1916).

[6] Hulett, *Phys. Rev.*, 32, **321** (1900).

[7] Nielsen and Brown, THIS JOURNAL, 49, **2423** (1927).

with copper. The amalgam, the supply of which was always kept under an acidified copper sulfate solution, had been previously put in the vessel after being washed. The glass stopper was then inserted and the solution brought to the proper concentration by repeatedly forcing out the solution with nitrogen and drawing in a solution of the required concentration. After drawing in each fresh supply, nitrogen was bubbled through the cell for a short time and the cell was shaken a few times. The solutions were often kept at about 40° to insure larger crystals and more rapid settling of the salt, but this seemed to have no influence on the results. The last addition of the solution was always below 25° so as to avoid any inrush of solution into the vessel when the stopcocks were opened for the potential measurements. The electrode was rotated in the thermostat four or five hours before being measured. Longer periods did not change the potential.

The hydrogen electrode consisted of a piece of platinized platinum foil. The electrode was prepared from clean platinum foil by electrolysis of a solution of pure chloroplatinic acid containing one per cent. of platinum. A four-volt battery was used and the current reversed every few minutes for one hour, as recommended by Ellis. The hydrogen entered the electrode vessel at the bottom and escaped through a trap. The platinum foil was only partially submerged in the solution. Hydrogen was prepared by electrolysis of sodium hydroxide solution and was passed through sulfuric acid before entering the preliminary washer which adjoined the electrode vessel in the thermostat and contained the same solution as the electrode vessel. Rubber connections were kept at a minimum and whenever they were used they were paraffined. In one of our measurements two hydrogen electrode vessels were used, the one receiving electrolytic hydrogen and the other hydrogen prepared from zinc and hydrochloric acid. The hydrogen from the latter source was passed through concentrated potassium hydroxide and over phosphorus pentoxide before entering the preliminary vessel. The difference in potential between the two electrodes was less than 0.01 millivolt. The hydrogen and cuprous chloride electrodes were joined through a beaker of the given solution, the arm of the cuprous chloride vessel having been protected by a plug during rotation in the thermostat. Both electrodes were set up four or five hours before being measured.

The hydrochloric acid solutions were made up from conductivity water, and weighed quantities were standardized with barium hydroxide, which in turn had been standardized with benzoic acid. Checks were obtained in all the titrations. All other apparatus and manipulations were the same as in our previous paper, such as "Type K" potentiometer, calibrated standard cell, thermostats, etc.

Electromotive Force of the Copper Amalgam Hydrogen Cell

In the following table the first column gives the number of the experiment, the second the molality of the acid used (moles per kilogram of water), and the third the partial pressure of hydrogen after correcting the

TABLE I

THE ELECTROMOTIVE FORCE OF THE CELL

Cu (in two-phase amalgam) + CuCl(s), HCl, H_2 at 25°

No.	m_{HCl}	*Pa*	E	γ_{HCl}
1	0.02029	700	−0.33615	0.893
2	.02029	689	− .33592	
3	.00757	695	− .38250	.933
4	.00757	698	− .38248	
6	.03564	697	− .30830	.874
6	.03564	692	− .30805	

barometer reading for temperature and subtracting the vapor pressure of the solutions, assumed equal to that of water. The fourth column gives the observed electromotive force and the fifth column the activity coefficient for the given molality of acid, interpolated from the table of Lewis and Randall.[8]

All six measurements were obtained in succession. The close agreement of each pair seems to be a fair check on the experimental work. Calculations based on these measurements will appear in the theoretical discussion.

Study of the Cell $CuCl(s)$, $CuCl_2(aq.)$, $Cl_2(g)$

Introduction.—This is of course the only combination of electrodes which we could use if we wish to avoid liquid junctions, since copper or mercury would cause precipitation of cuprous chloride from the cupric chloride solutions. The $CuCl$-$CuCl_2$ electrode was studied by Luther and Wilson,[3] who measured the cell $CuCl$, $CuSO_4$ and KCl (each $MV/20$), N. E. Obviously we cannot use this measurement in our calculations.

Experimental Work.—With the exception of the preparation of the chlorine electrodes, all procedure was the same as given above, including preparation and rotation of the $CuCl$-$CuCl_2$ electrodes. In setting up the chlorine electrodes we followed essentially the method of Lewis and Rupert.[9] The bulb of a separatory funnel was sealed into the neck of a carboy by means of de Khotinsky cement. A mixture of air and chlorine was forced into the carboy under pressure, the partial pressure of air being at least ten times that of chlorine. The air was dried before entering the carboy and the chlorine was taken directly from a cylinder. The carboy contained some calcium chloride to serve as a drying agent. The chlorine electrode vessels were essentially like the hydrogen electrode vessels described above, except that bright platinum-iridium foil was used instead of platinum black.

The cupric chloride solutions were made up gravimetrically, with conductivity water, from a stock solution which had been standardized iodimetrically. The stock solution had been made up from crystals of the dihydrate, obtained by recrystallization of the best C. P. product from a solution containing excess of hydrochloric acid. These crystals were dried in a vacuum desiccator containing soda-lime. The solutions were kept in Pyrex flasks, over which watch glasses had been sealed with paraffin. The saturated electrode was set up by adding excess of the dihydrated salt to the electrode vessel at the time it was set up. The more dilute solutions contained about a drop of nitric acid in 500 cc. of solution to prevent the formation of a green precipitate, probably a basic salt.

In order to standardize the chlorine mixture the stem of the separatory funnel leading from the carboy was divided by means of a Y-junction. The mixture was thus allowed to go simultaneously through one pass into an electrode vessel containing the required cupric chloride solution and through the other pass into an electrode vessel containing 0.0478 M hydrochloric acid. The hydrochloric acid electrode was measured against a hydrogen electrode with the same hydrochloric acid solution. The Cl_2-$CuCl_2$ electrode was measured against the $CuCl$-$CuCl_2$ electrode, prepared similarly to the Cu-$CuCl$ electrodes described above. The two latter electrodes of course con-

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[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York City, 1923.

[9] Lewis and Rupert, THIS JOURNAL, 33, 299 (1911).

tained cupric chloride of the same molality. The cells were measured almost simultaneously, after sufficient time had elapsed to insure equilibrium in all the electrode vessels. In other words, we obtained simultaneously the electromotive forces corresponding to both the following reactions

$$\tfrac{1}{2}Cl_2(p) + \tfrac{1}{2}H_2\ (700\ \text{mm.}) = HCl\ (0.0478\ M) \qquad (1)$$

$$\tfrac{1}{2}Cl_2(p) + CuCl(s) = CuCl_2\ (\text{given molality } m) \qquad (2)$$

The data of Lewis and Rupert were then used to determine the partial pressure of the chlorine in each case. The electrodes were joined only long enough to be measured and adjustments were such as to avoid flow from one to the other.

Electromotive Force of the Cell.—In the following table the first column gives the number of the experiment, the second the molality of the cupric chloride, the third the measured electromotive force of the hydrochloric acid cell and the fourth that of the cupric chloride cell. The partial pressure of hydrogen in this series was assumed constant at 700 mm.

TABLE II

THE ELECTROMOTIVE FORCES OF THE CELL H_2 (700 mm.), HCl (0.0478 *M*), Cl_2(p), AND THE CELL CuCl(s), $CuCl_2(m)$, Cl_2(p) AT 25°

No.	m_{CuCl_2}	E_{HCl}	E_{CuCl_2}
7	0.01	1.4791	1.0900
8	.01	1.4787	1.0893
9	.02	1.4812	1.0479
10	.02	1.4809	1.0476
11	.2	1.4835	.9136
12	.2	1.4745	9043
13	.2	1.4760	.9066
14	1	1.4812	.7958
15	1	1.4785	.7928
16	5.82[10]	1.4787	.6170

Calculations and Theoretical Discussion

The Copper-Cuprous Chloride Electrode

Since the reaction which occurs in the cell (Table I) is Cu (in two-phase amalgam) + H^+Cl^- (at m) = CuCl(s) + $\tfrac{1}{2}H_2$ (at p), the relation between the observed e.m.f. E and that E_0 calculated for the case in which H^+, Cl^- and H_2 have unit activity is given by the expression

$$E_0 = E + 0.05915 \log \frac{(p/760)^{1/2}}{a_{H^+} \cdot a_{Cl^-}} \qquad (3)$$

in which the a's refer to the given activities. The geometric mean activity of the ions is equal to the molality m_{HCl} multiplied by the activity coefficient γ_{HCl}, provided the solubility of cuprous chloride is small, and the expression becomes

$$E_0 = E + 0.05915 \log \frac{(p/760)^{1/2}}{m^2\gamma^2} \qquad (4)$$

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[10] From the solubility measurements of Reicher and van Deventer, *Z. physik. Chem.*, 5, 559 (1890).

The values of E_0 thus calculated are given in the third column of Table III, the first column giving the number of the experiment and the second the molality of hydrochloric acid for comparison of the data.

There are, however, two factors which influence the concentration of chloride ion in the hydrochloric acid solutions. The first is the formation of the complex ion $CuCl_2^-$, for which Noyes and Chow[4] found, at 25°, the relation

$$(CuCl_2^-)/(Cl^-) = 0.0661 \qquad (5)$$

the parentheses denoting concentrations. Activities may be substituted for the concentrations in accordance with the principle[8,16] that the activity coefficient in dilute solutions is determined chiefly by the total ionic strength and is nearly the same for all ions of unit charge. In **all** that follows, parentheses will denote activities. The second factor is the reaction

$$2CuCl(s) = Cu^{++} + 2Cl^- + Cu \qquad (6)$$

In the case of the most concentrated hydrochloric acid solutions (Table I), Equation 5 has a far greater effect than Equation 6 on the concentration of chloride ion. This will be evident in the subsequent calculations. Assuming that in the most concentrated solution (Cl^-) is reduced in the ratio 1/1.0661 by complex formation, and anticipating Equation 14, we shall correct the value of E_0 for the most concentrated solution by the amount 0.828.0.5915 log 1.0661 or 0.0013 volt and write[11]

$$Cu + Cl^- = CuCl(s) + E^-;\ \Delta F^\circ_{298} = 0.1298\,F \qquad (7)$$

By Equation 22,

$$CuCl(s) = Cu^{++} + Cl^- + E^-;\ \Delta F^\circ_{298} = 0.5758\ F \qquad (8)$$

Combining,

$$2CuCl(s) = Cu^{++} + 2Cl^- + Cu;\ \ \Delta F^\circ_{298} = 0.4460F = -RT\ln(Cu^{++})(Cl^-)^2 \qquad (9)$$

Then

$$(Cu^{++})(Cl^-)^2 = \text{antilog}\ \frac{-0.4460}{0.05915} = 2.82 \times 10^{-8} \qquad (10)$$

If we assume that for every Cu^{++} ion produced by Equation 6, two Cl^- ions are produced, and for every $CuCl_2^-$ ion produced, one Cl^- ion disappears, then the activity of Cl^- ion in the electrode chamber is given by

$$\begin{aligned}(Cl^-) &= \gamma_{Cl^-}\, m_{Cl^-} - (CuCl_2^-) + 2\gamma_{Cl^-}(Cu^{++})/\gamma_{Cu^{++}} \\ &= \gamma_{Cl^-}\, m_{Cl^-} - 0.0661(Cl^-) + \frac{2 \times 2.82 \times 10^{-8}}{(Cl^-)^2} \times \gamma_{Cl^-}/\gamma_{Cu^{++}} \qquad (11)\end{aligned}$$

from Equations 5 and 10. We may assume that the individual ion activity coefficients are the same for all ions of unit charge and are those given in Table I. The coefficients for Cu^{++} are taken from the table of Lewis and Randall for individual ions and are given in the fourth column of Table III. The fifth column gives the solution of Equation 11. It has been assumed that all the dissolved cuprous chloride is in the form of the complex ion.

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[11] **The symbols and conventions used in this paper are those of Lewis and Randall, *See* Note 8.**

Before we can correct our potentials, we must consider another effect, namely, the summation of free energies of dilution and concentration in the composition gradient portion, which occur when the cell operates and which give rise to the so-called "liquid potential." The expressions for the electromotive forces of concentration cells have been derived by integration methods,[12] and their form indicates that for convenience a sharp boundary may be assumed. Since electrical neutrality will be maintained chiefly by ions present in the largest concentration, we may assume that hydrogen ion and chloride ion are the chief substances transferred. Since the concentration of hydrogen ion is the same on both sides of the junction, the free-energy change, due to transference, accompanying the passage of one Faraday is manifested in a potential

$$E_L = t_A \cdot 0.05915 \log a_1/a_2 \qquad (12)$$

where t_A is the transference number of the anion, and a_1 and a_2 are the activities of chloride ion on the two sides of the junction. If all the transference were accomplished by hydrogen ions, our values of E_0 would have to be corrected by the amount

$$\Delta E_T = 0.05915 \log \gamma m/(\mathrm{Cl}^-) \qquad (13)$$

since all the chloride ion formed would be at activity (Cl^-) rather than at γm. The effect of Equation 12 is to offset in part that of Equation 13, and we therefore obtain the value

$$AE = t_C \cdot 0.05915 \log \gamma m/(\mathrm{Cl}^-) \qquad (14)$$

to be added to the values of E_0. The cation transference number (t_C) is taken as 0.828.[13] The values of AE are given in the sixth column of Table III, and the corrected values of E_0 in the seventh column. The values of γm used in calculating E_0 are given in the eighth column for comparison with those of (Cl^-).

TABLE III

CALCULATED VALUES FOR THE COPPER AMALGAM-CUPROUS CHLORIDE ELECTRODE

No.	m_{HCl}	E_0	$\gamma_{\mathrm{Cu}^{++}}$	(Cl^-)	AE	E_0'	γm
1	0.02029	−0.13116	0.53	0.01731	0.0010	−0.1302	0.01813
2	.02029	− .13113	.53	.01731	.0010	− .1301	,01813
3	.00757	− .12915	.63	.00795	− .0026	− .1317	.00706
4	.00757	− .12907	.63	.00795	− .0026	− .1317	.00706
5	.03564	− .13116	.48	.02932	.0013	− .1299	.03115
6	.03564	− .13100	.48	.02932	.0013	− .1297	.03115

The calculated values of (Cl^-), as compared with γm, show that in the case of the most concentrated solution the effect of complex formation is

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[12] See ref. 8, p. 337 and ref. 16, p. 782 (chapter by Harned).

[13] Partington, "Conductance, Ionization, and Ionic Equilibria," p. 546. Chapter XI of Taylor's "Treatise on Physical Chemistry," D. Van Nostrand Co., New York City, 1925.

predominant, while in the case of the most dilute solution the effect of formation of cupric chloride is predominant. This is qualitatively verified in the experiments. The experimental data show that the formation of cupric chloride did not take place to the extent calculated. This fact is somewhat surprising, considering the constancy and reproducibility of our electrodes. It might be mentioned that an error in the activity coefficient of Cu^{++} would have a marked effect on the calculated values of (Cl^-). We shall take the value of $\mathbf{E}_0'$ for the most concentrated solution, and regard this as the standard potential of copper amalgam and cuprous chloride in the presence of chloride ion at unit activity. This value is probably correct to within two- or three-tenths of a millivolt. We therefore write

$$\text{Cu (in two-phase amalgam)} + Cl^- = CuCl(s) + E^-;\ E^\circ = -0.1298 \text{ volt,}$$
$$\Delta F^\circ_{298} = 23074 \cdot 0.1298 \text{ cal.} = 2995 \text{ cal.} \qquad (15)$$

This value is to be used in calculating free energies and equilibrium constants. The values of $\mathbf{E}_0$ in Table III may be used when the electrode is employed as a reference electrode with a given hydrochloric acid solution.

Our value for the standard potential of this electrode is to be compared with that of Noyes and Chow,[4] who found —0.1200 volt for the standard potential, using copper plated on platinum. The standard potential of the amalgam in copper sulfate, as found in our previous paper, is —0.3502 volt. Lewis and Randall give —-0.3448 volt, based on the work of Lewis and Lacey,[14] for the standard potential of a copper sponge prepared by rapid electrolysis of copper sulfate on a platinum point. We have been unable to produce copper of as low reducing power as this by any method whatever, but this copper would give —0.1244 volt for the standard potential of the copper-cuprous chloride electrode. Comparison of this value with that of Noyes and Chow, ignoring the slight error introduced by the liquid junction, indicates that the smooth copper plate which they used contained energy stored in the form of distortion from a more stable form of copper.

Calculations: The Cuprous Chloride-Cupric Chloride Electrode

The reaction which occurs in the copper chloride cells (Table II) is

$$CuCl(s) + \tfrac{1}{2}Cl_2 \text{ (at p)} = CuCl_2 \text{ (at m)} \qquad (16)$$

That which occurs in the hydrochloric acid cell is

$$\tfrac{1}{2}H_2 \text{ (at 700 mm.)} + \tfrac{1}{2}Cl_2 \text{ (at p)} = HCl \text{ (at 0.0478 M)} \qquad (17)$$

The electromotive force that would be given by the latter cell if all substances were. at unit activity is 1.3594 volts, according to the tables of Lewis and Randall, based on the work of Lewis and Rupert.[9] If only the chlorine were at a fugacity or activity of one atmosphere and the other substances at the concentrations indicated by Equation 17, the electromotive force would be

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[14] Lewis and Lacey, THIS JOURNAL, 36, 804 (1914).

$$1.3594 + 0.05915 \log \frac{(700/760)^{1/2}}{(0.861)^2(0.0478)^2} = 1.5222 \text{ volts}$$

the activity coefficient for the given hydrochloric acid being taken as 0.861 from Lewis and Randall. In order, therefore, to find the electromotive force that would be given by the copper chloride cells if the chlorine were at unit activity, the difference between the value 1.5222 and the observed value $\mathbf{E}_{\mathrm{HCl}}$ (Table II) must be added to the corresponding value of $\mathbf{E}_{\mathrm{CuCl_2}}$, since the same chlorine mixture was used in the two corresponding cells. These corrected values $\mathbf{E}_0$ for the copper chloride cells are given in the third column of Table IV, the first giving the number of the experiment and the second the molality of the cupric chloride used. The hydrolysis of the chlorine is negligible at the partial pressures used. The mean value of $\mathbf{E}_0$ at each molality is given in the fourth column.

As in the case of our copper-cuprous chloride electrodes, the concentration of chloride ion is affected by the formation of $CuCl_2^-$ and, in the case of the more concentrated solutions, by the formation of much $CuCl_3^-$ and various chloro-cuprate ions. We shall neglect all factors except the formation of $CuCl_2^-$, although these factors are by no means completely negligible in the concentrated solutions. If we assume that the concentration of chloride ion is cut down by cuprous chloride in the ratio 1/1.0661 in accordance with Equation 5, then the chlorine would become chloride ion at molality $2m_{\mathrm{CuCl_2}}$ and the cuprous chloride would form chloride ion at molality $2m_{\mathrm{CuCl_2}}/1.0661$. If all the transference were accomplished by positive ions, the chloride ions formed would remain at these molalities, and the value 0.05915 log 1.0661 would have to be subtracted from the values of $\mathbf{E}_0$ in Table IV to find the e.m.f. that would be obtained if the concentration of chloride ion were really $2m_{\mathrm{CuCl_2}}$. When the cell operates, however, some chloride ion is transferred from the chlorine electrode vessel to the cuprous chloride solution, which is more dilute with respect to chloride ion, and this has the effect of increasing the electromotive force by the amount $t_{\mathrm{A}} \cdot 0.05915 \log 1.0661$, where t_{A} is the transport number of chloride ion. We are assuming a sharp boundary, as explained in the previous section, and a constant activity coefficient at any one molality. We must accordingly subtract the value

$$AE = (1 + t_{\mathrm{A}})\ 0.05915 \log 1.0661 \qquad (18)$$

from the values of $\mathbf{E}_0$ to find the e.m.f. that would be obtained if the concentration of chloride ion were actually $2m_{\mathrm{CuCl_2}}$. These corrected e.m.f.'s, $\mathbf{E}'_0$, are given in the seventh column of Table IV.

It might be argued that the $CuCl_2^-$ ion cannot be regarded as a foreign ion, since storing up an ion in the form of a complex might not be qualitatively different from storing it up as a hydrated ion or in any other unactivated form. In our treatment it is, of course, assumed that, of the total chloride ion present, the instantaneous fraction in active equilibrium with solid CuCl and cuprous ion is reduced very nearly in the ratio 1/1.0661 by complex formation.

In dilute solutions we shall take t_A as 0.6 by analogy with various electrolytes. In very concentrated cupric chloride solutions the transport numbers for the anion become greater than unity, owing to the formation of chloro-cuprate ions, according to the work of Kohlschütter.[15] Since we are regarding complex ions as foreign ions, our value of t_A must be the fraction of the current carried by the chloride ions alone, and we have selected the rather arbitrary values given in the fifth column of Table IV. This procedure ignores the fact that other ions are transferred to different environments, but the corrections are small and at any rate the presence of cuprous chloride makes the molalities and the calculated activity coefficient doubtful in the most concentrated solutions. The values of AE calculated from Equation 18 are given in the sixth column and the corrected values of E_0 in the seventh column, these corrected values, E'_0, having the significance stated above.

From the reaction of Equation 16, the following relation must hold between the values of E'_0

$$E'_{0x} - E'_{0y} = 0.05915 \log \frac{(\gamma_y m_y)^3}{(\gamma_x m_x)^3} \qquad (19)$$

in which the x and y refer to the number of the experiment and $\gamma m = \sqrt[3]{(Cu^{++})\,(Cl^-)^2}$ where the parentheses denote activities. The "mean activity coefficient," γ, as calculated by Equation 19, is given in the eighth column of the table, that for the 0.01 molal solution being calculated from the table of individual ion coefficients of Lewis and Randall.

TABLE IV

CALCULATED VALUES FOR THE CUPROUS CHLORIDE-CUPRIC CHLORIDE ELECTRODE

No.	m_{CuCl_2}	E_0	Mean E_0	t_A	ΔE	E'_0	γ_{CuCl_2}
7	0.01	1.1328	1.1330	0.6	0.0026	1.1304	(0.700)
8	.01	1.1331					
9	.02	1.0889	1.0889	.6	.0026	1.0863	.620
10	.02	1.0889					
11	.2	.9523	.9523	.5	.0025	.9498	.365
12	.2	.9520					
13	.2	.9528					
14	1	.8368	.8367	.4	.0023	.8344	.326
15	1	.8365					
16	5.82[11]	.6605	.6605	.2	.0020	.6585	.55

Various causes may be given for the trend of the activity coefficient. The "electrostatic virial" theory of Debye and Hückel[16] as extended by Hiickel''

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[15] Kohlschütter, *Ber.*, 37, 1153 (1904).

[16] Debye and Hiickel, *Physik. Z.*, 24, 185 (1923). See also Noyes, THIS JOURNAL, 46, 1080 (1924).

[17] Hiickel, *Physik. Z.*, 26, 93 (1925)

probably accounts for the greater portion of the trend. Scatchard[18] has suggested that hydration may be another factor in determining the values of γ. Many factors enter into consideration for the concentrated cupric chloride solutions, including hydration, formation of ionic and molecular complexes, etc. The factors are probably linked up with the color changes, the color changing from blue to green or from dark green to a dark reddish-brown on saturation with cuprous chloride, in the case of the most concentrated solutions. The molality, and hence the calculated activity coefficient, is somewhat in doubt in the case of the saturated solution, owing to the large solubility of cuprous chloride. Other complicating factors have been mentioned previously.

Since the cell reaction for this set of experiments is that given by Equation 16, we may calculate the standard potential of the cuprous chloride-cupric chloride electrode by the relation

$$E^\circ = E_0' + 0.05915 \log (Cu^{++}) (Cl^-)^2 + E^\circ_{Cl_2} \qquad (20)$$

using any value of E_0' and the corresponding values for the activities. This value, E^0, is the value which, if the standard potential of the chlorine electrode be subtracted from it, gives the electromotive force that would be obtained from our cupric chloride cells if the activity of both ions were unity. Using the values for the 0.01 molal solution, including the "mean activity coefficient" of 0.700 and the standard potential of the chlorine electrode given previously, Equation 20 becomes

$$E^\circ = 1.1304 + 0.05915 \log 4(0.700 \cdot 0.01)^3 - 1.3594 \qquad (21)$$

We may therefore write

$$CuCl(s) = Cl^- + Cu^{++} + E^-;\ E^\circ = -0.5758 \text{ volt},$$
$$\Delta F^\circ_{298} = 23074 \cdot 0.5758 = 13{,}285 \text{ cal.} \qquad (22)$$

This value, as well as our activity coefficients, is slightly in doubt, owing to the calculation of γ at 0.01 M from individual ion coefficients. The values of E_0 may be employed when this electrode is used as a reference electrode.

Standard Free Energies Based on Both Electrodes

Subtracting the standard chlorine potential from Equation 22, we obtain

$$CuCl(s) + \tfrac{1}{2}Cl_2(g) = CuCl_2 \text{ (aq. at unit activity)}$$
$$\Delta F^\circ_{298} = -(1.3594 - 0.5758)23074 = -18{,}080 \text{ cal.} \qquad (23)$$

Subtracting the standard potential of chlorine from Equation 15, we obtain

$$Cu \text{ (in two-phase amalgam)} + \tfrac{1}{2}Cl_2(g) = CuCl(s)$$
$$\Delta F^\circ_{298} = -(1.3594 - 0.1298)23074 = -28{,}370 \text{ cal.} \qquad (24)$$

Combination of Equations 23 and 24 gives

$$Cu \text{ (in two-phase amalgam)} + Cl_2(g) = CuCl_2 \text{ (aq. at unit activity)}$$
$$\Delta F^\circ_{298} = -46{,}450 \text{ cal.} \qquad (25)$$

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[18] Scatchard, THIS JOURNAL, 47, 2096 (1925).

From the value of E_0 for the saturated cupric chloride solution we may obtain the free energy of the dihydrate. The equation is

$$CuCl(s) + \tfrac{1}{2}Cl_2 \text{ (1 atm.)} + 2H_2O \text{ (in sat. } CuCl_2 \text{ sol.)} = CuCl_2{\cdot}2H_2O(s)$$
$$E = 0.6605 \text{ volt} \qquad (26)$$

From the vapor-pressure data of Ewan and Ormandy,[19] the activity of the water is found to be 0.65. Hence the value 0.05915 log $(0.65)^2$, or —0.0221, has to be subtracted from Equation 26, and we obtain

$$CuCl(s) + \tfrac{1}{2}Cl_2(g) + 2H_2O\ (1) = CuCl_2{\cdot}2H_2O(s)$$
$$\Delta F^\circ_{298} = -23074\ (0.6605 + 0.0221) = -15{,}750 \text{ cal.} \qquad (27)$$

Combination with Equation 24 gives

$$Cu \text{ (in two-phase amalgam)} + Cl_2(g) + 2H_2O(l) = CuCl_2{\cdot}2H_2O(s):$$
$$\Delta F^\circ_{298} = -44{,}100 \text{ cal.} \qquad (28)$$

From Equation 9,

$$2\ CuCl\ (s) = CuCl_2\ (aq.) + Cu \text{ (in two-phase amalgam);}$$
$$\Delta F^\circ_{298} = 23074.0.4460 = 10{,}290 \text{ cal.} \qquad (29)$$

Summary

By measurements of the cell Cu (in two-phase amalgam), CuCl(s), HCl, H_2, the standard potential of the copper amalgam-cuprous chloride electrode was determined (Equation 15). The results were compared with those of other investigators.

By measurements of the cell Cl_2 (at low pressures), $CuCl_2$ (aq.), CuCl(s), the standard potential of the cuprous chloride-cupric chloride electrode was determined (Equation 22), as well as the activity of cupric chloride over a limited range (Table IV).

To insure reliable results, copper amalgam was used instead of metallic copper, oxygen was excluded and the electrodes were rotated in the thermostat. Chemical reactions affecting the concentration of chloride ion were treated mathematically and corrections made for them. Views regarding the liquid junctions and the trend of the activity coefficients were expressed.

The standard free energies of the two solid chlorides and of aqueous cupric chloride were calculated (Equations 24, 25 and 28) as well as the standard free energies of several other reactions.

LINCOLN, NEBRASKA

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[19] Ewan and Ormandy, J. Chem. *Soc.*, 61, 775 (1892).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AMHERST COLLEGE]

COPPER SULFATE AS THE DEACON CHLORINE CATALYST?[1]

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Introduction

If we may judge from the literature, there is considerable doubt concerning the role of cupric sulfate when employed in the catalytic process of Deacon for the direct oxidation of gaseous hydrogen chloride. In the First Report of the Committee on Contact Catalysis,[2] following a discussion of a possible mechanism for cupric chloride catalyst, we find the statement, "when we start with copper sulfate as the catalytic agent, which may be done, the whole thing becomes hopelessly complicated." Levi and Bettoni[3] suggest an intermediate hydrate formation

$$CuSO_4 + 2HCl + {}^1/_2O_2 = CuSO_4{\cdot}H_2O + Cl_2$$
$$CuSO_4{\cdot}H_2O = CuSO_4 + H_2O$$

Now Hensgen[4] and others have shown that many of the metal sulfates are attacked by dry hydrogen chloride gas to form the corresponding chlorides and liberate sulfuric acid. This work suggests the possibility of the conversion of cupric sulfate according to the following equation

$$CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$$

If this be true, then it is probable, if we start with copper sulfate in the Deacon Process, that the copper chloride formed is the catalyst, and the mechanism is the same as if copper chloride had been used initially.

The available data for the action of hydrogen chloride on copper sulfate are rather controversial and indefinite as regards experimental conditions, especially temperature. Hensgen finds an addition compound of $CuSO_4{\cdot}2HCl$ (approximately) by the action of dry hydrogen chloride on anhydrous copper sulfate at room temperature. He suggests that this compound, $CuSO_4{\cdot}2HCl$, plays an important role in the Deacon reaction. In a later article,[5] Hensgen shows that 2.18 moles of hydrogen chloride are absorbed per mole of pentahydrated copper sulfate, giving this observation to support the following equation

$$CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$$

Other writers[6,7] find addition compounds or partial conversion to copper chloride. With the exception of one experiment by Hensgen, all these

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[1] This paper is the report of work previously cited in the Fourth Report of the Committee on Contact Catalysis, Taylor, J. *Phys. Chem.*, 30, 145 (1926).

[2] Bancroft, J. *Ind.* Eng. *Chem.*, *14,* 328 (1922).

[3] Levi and Bettoni, *Gazz. chim. ital.*, *35 (I),* 320 (1905).

[4] Hensgen, *Ber.*, 9, 1675 (1876).

[5] Hensgen, *Ber.*, 10, 259 (1877).

[6] Latchinoff, J. *Russ. Phys.-Chem. Soc.*, 20, 585 (1888).

[7] Colson, *Compt. rend.*, 124, 82 (1897).

reactions were run at temperatures well below that used in the Deacon Process.

To clear up any doubt, it seemed desirable to determine whether hydrogen chloride gas alone, or admixed with oxygen, does indeed quantitatively liberate sulfuric acid from copper sulfate with the concomitant formation of a chloride or oxychloride of copper, this test to be made at about 450°, the temperature used in the Deacon Process.

Preparation of Materials

The hydrogen chloride gas was prepared by dropping concentrated sulfuric acid on a solution of C. P. concentrated hydrogen chloride. The gas bubbled through two wash bottles containing concentrated hydrogen chloride solution, and thence passed through calcium chloride towers. The train of wash bottles and towers served effectively to remove any mechanically carried sulfuric acid. By counting the bubbles in the wash bottles it was possible to estimate rate of flow.

The oxygen was supplied from a commercial tank, passed through a bubbler containing paraffin oil to estimate rate of flow and thence through calcium chloride.

The copper sulfate was prepared by heating C. P. pentahydrated copper sulfate to about 450° in a stream of dry air. Analysis for copper and sulfate showed the product to have the composition of anhydrous cupric sulfate.

Procedure

In his experiments, Hensgen tested the reaction, $CuSO_4 + HCl$, by determining the composition of the residual copper salt. At the temperature employed by us cupric chloride is partially dissociated into cuprous chloride and chlorine. Moreover, in the experiments where oxygen was mixed with the hydrogen chloride, some oxychloride was probably formed. The residual copper salt would be a mixture of cupric and cuprous chloride and, in some experiments, probably oxychloride of copper $CuO \cdot CuCl_2$. Hence it was thought better to test the completeness of the reaction, $CuSO_4 + 2HCl = CuCl_2 + H_2SO_4$, by determining the sulfuric acid evolved.[8]

Hydrogen chloride alone, or hydrogen chloride mixed with oxygen, was passed over a weighed sample of anhydrous copper sulfate contained in a hard glass tube which was electrically heated to about 450° as measured by a nitrogen filled mercury thermometer. When hydrogen chloride alone was used, the rate of gas flow was estimated at 12 liters per hour; when the mixture was used, the rate was 15 liters per hour. In these experiments on the liberation of sulfuric acid from the sulfate, a

[8] At 450°, the sulfuric acid is, of course, largely dissociated into sulfur trioxide and water.

variation of 20° was found to have no effect on the total amount of sulfuric acid liberated; hence it was considered safe to keep the temperature between 440 and 460°. Preliminary to a run, the tube was swept out with dry hydrogen chloride and was brought to the desired temperature. The tube was then opened at the end where the gases were admitted, the sample of copper sulfate contained in a porcelain boat was quickly inserted and the tube was closed. The sulfuric acid in the effluent gas was absorbed in a train of four spiral wash bottles filled with concentrated hydrogen chloride solution. Concentrated hydrogen chloride was here preferred to water because its use eliminated the danger that the solution might suck back due to the too rapid solution of hydrogen chloride gas. The long train was found necessary to effect the complete absorption of the sulfuric acid. After action was complete, the liquid contained in the wash bottles was boiled down to a small volume to expel most of the hydrogen chloride. The residual liquid was neutralized by ammonia, then made slightly acid by hydrogen chloride, diluted and analyzed for sulfate content by precipitation of barium sulfate.

Results

Action of Hydrogen Chloride Alone.—The white color of the anhydrous copper sulfate gradually changed to a dirt-brown, resembling that of anhydrous cupric chloride. After five to six hours the mass began to liquefy and sublimed cuprous chloride was apparent on the cooler portions of the tube. At this stage, and not before, evolution of sulfuric acid was found to be complete.

Table I gives a comparison between the weight of barium sulfate calculated according to the equation, and the actual weight found by analysis.

TABLE I

ACTION OF HYDROGEN CHLORIDE ON COPPER SULFATE AT 450° (APPROX.)

Sample	$CuSO_4$ taken, g.	$BaSO_4$ calcd., g.	$BaSO_4$ found, g.	Yield of H_2SO_4, %
1	0.3609	0.5377	0.5401	100.4
2	.2166	.3167	.3188	100.6
3	.3046	.4454	.4484	100.6

Action of Hydrogen Chloride—Oxygen Mixture.—In order to duplicate the conditions of the Deacon Process, a test was made of the action of a mixture of hydrogen chloride and oxygen in approximate ratio, by

TABLE II

ACTION OF HYDROGEN CHLORIDE MIXTURE ON COPPER SULFATE AT 450° (APPROX.)

Sample	$CuSO_4$ taken, g.	$BaSO_4$ calcd., g.	$BaSO_4$ found, g.	Yield of H_2SO_4, %
1[a]	0.2501	0.3657	0.3622	99.3
2	.2280	.3334	.3342	100.2
3	.3200	.4689	.4681	99.8

[a] Crucible cracked—possibly slight loss.

volume, of 4:1. The observations concerning color change, time for completion, etc., were not sensibly different from those when hydrogen chloride alone was used. The results are tabulated in Table II.

Rate of Evolution of Sulfuric Acid.—In order to get an estimate of the course of the reaction with time, the absorption train was replaced at various time intervals by a duplicate and the amount of sulfuric acid evolved during the various intervals was determined by separate barium sulfate precipitations. The anhydrous copper sulfate used here weighed **0.2707** g.; the yield of barium sulfate should, therefore, have been **0.3960** g. when conversion was complete. The sum of the weights in Col. 2 of Table III is 0.3985 g. Col. **3** lists the percentages of sulfuric acid evolved in the various time intervals and Col. 4, the total percentage at the end of each interval.

TABLE III

RATE OF EVOLUTION OP SULPURIC ACID

Time interval, minutes	$BaSO_4$ found, g.	for interval, %	Total H_2SO_4, %
0–22	0 0347	8.77	8.77
22–60	.0809	20.22	28.99
60–100	.0460	11.62	40.61
100–140	.0450	11.37	51.98
140–230	,1527	38.75	90.73
230–380	.0392	9.88 .	100 61

It will be observed that the copper sulfate was not immediately decomposed. After 140 minutes only 52% had yielded up its sulfate, and **9.3%** remained unchanged even after 230 minutes or almost four hours. The action was complete, however, at the end of six hours. This rate of evolution of sulfuric acid should be taken only as a roughly quantitative statement. Obviously the rate would be influenced by many factors such as amount of surface of copper sulfate exposed, size and shape of containing tube and variations in temperature.

The foregoing data prove definitely that a quantitative yield of sulfuric acid is obtained by heating copper sulfate to 450° in a stream of hydrogen chloride or hydrogen chloride-oxygen mixture. After six hours' time no sulfate is left in the catalyst mass. Hence, if we start with copper sulfate in the Deacon Process, the catalyst, after six hours' time, must be copper chloride and cannot be copper sulfate.

In one experiment the following test was made on the effluent gas produced when hydrogen chloride—oxygen mixture passed over copper sulfate. The gas stream was divided in two parts. One part bubbled through barium chloride solution to test for sulfate, the other through potassium iodide to test for chlorine. As nearly as could be determined, the evolution of sulfuric acid and the production of chlorine began almost simultaneously at the end of about five minutes from the time the catalyst was inserted. This time was doubtless needed to bring the catalyst to the temperature of the furnace. Since chlorine was not produced before the sulfuric acid began to come off, it is needless to assume that copper sulfate acted as catalyst even at the very start of the action; because as soon as a very small amount of copper sulfate was converted into chloride, the latter could function as the catalyst.

Summary

1. At 450°, sulfuric acid is quantitatively displaced from copper sulfate by the action of dry hydrogen chloride gas alone, or admixed with oxygen. We may assume that the residual salt is entirely in the form of copper chloride or oxychloride.
2. Hence the mechanism of the Deacon Process when copper sulfate is used as the initial form of the catalyst is no more complicated than it is when cupric chloride is used initially.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

VAPOR PRESSURE DATA FOR ISOPROPYL ALCOHOL AND TERTIARY BUTYL ALCOHOL

BY GEORGE S. PARKS AND BERNARD BARTON

RECEIVED SEPTEMBER 6, 1927 PUBLISHED JANUARY 5, 1928

The literature apparently contains no data for the vapor pressures of *iso*propyl alcohol and tertiary butyl alcohol over a range of temperatures. In view of the increasing importance of these substances, the present investigation was undertaken to remedy the deficiency.

Experimental Part

Two methods for measuring the vapor pressures of the liquids were employed. From 20 to 90° the static method of Smith and Menzies[1] was utilized. The isoteniscope was of the U type and was immersed in a small hand-regulated thermostat. The temperatures were measured to 0.01° by a thermometer which had been calibrated against a similar thermometer standardized by the United States Bureau of Standards. The manometer was U-shaped, with the evacuated side permanently connected to a high-vacuum pump consisting of a bulb of activated charcoal immersed in liquid air.

A second static method, developed in this Laboratory, was employed in measurements on *iso*propyl alcohol from 0 to 30° and on undercooled *tert.*-butyl alcohol at 20 and 25°. In this case our apparatus was essentially similar in principle to that described by Johnston,[2] although at the

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[1] Smith and Menzies, THIS JOURNAL, 32, 1419 (1910).

[2] Johnston, *Z. physik. Chem.*, 62,333 (1908).

time of its development we were unaware of anything similar in the literature. However, we dispensed with the large manometer employed by Johnston, as none of our pressure readings by this method were above 70 mm. For a pump we again used a tube of activated charcoal in liquid air. Manometer readings were made by a brass cathetometer reading to 0.05 mm.

The *iso*propyl alcohol was prepared from "refined" material supplied by the Eastman Kodak Co. This was subjected to four treatments and distillations with lime in the ordinary manner and then to two very careful fractionations. The middle 50% was used for the measurements. It had a density of 0.78091 at 25°/4°, corresponding to a purity of 99.97% on the basis of the criteria[3] previously employed.

The *tert.*-butyl alcohol was a refined material (m. p. 12°) given to us by the Petroleum Chemical Corporation. It was first subjected to ten fractional crystallizations. The resulting product was treated with lime and distilled, then treated with a small amount of metallic sodium and redistilled. The distillate thereby obtained was next subjected to fifteen additional fractional crystallizations. The final product had a freezing point of 25.50°.

Three or more sets of determinations were carried out upon each alcohol by the two-different methods, the measurements being made over the temperature ranges previously indicated at intervals of approximately 5°. The results obtained were in general very concordant. The vapor pressure values for each alcohol were plotted against the corresponding temperatures; a smooth curve was then drawn and from this the vapor pressures were read at exactly five degree intervals. These are the results appearing in Table I. In the case of the isopropyl alcohol they are probably accurate to within 0.2 mm. at the lower temperatures and to within 0.8 mm. at the highest temperatures; for the *tert.*-butyl alcohol the errors may be 50% greater than these, owing to more difficulty in the purification

TABLE I

VAPOR PRESSURE DATA

Temp., °C.	Vapor pressure of		Temp., °C.	Vapor pressure of	
	C_3H_7OH	C_4H_9OH		C_3H_7OH	C_4H_9OH
0.00	**8.9**	...	**50.00**	**176.8**	**174.3**
5.00	**12.1**	...	**55.00**	**227.4**	**224.2**
10.00	**17.0**	...	**60.00**	**288.5**	**285.2**
15.00	**23.8**	...	**65.00**	**363.1**	**358.2**
20.00	**32.4**	**30.6**	**70.00**	**454.8**	**447.3**
25.00	**44.0**	**42.0**	**75.00**	**561.4**	**553.2**
30.00	**59.1**	**56.9**	**80.00**	**691.8**	**679.4**
35.00	**78.9**	**76.3**	**85.00**	**845.6**	**826.3**
40.00	**105.6**	**102.3**	**90.00**	**1020.7**	**996.2**
45.00	**136.8**	**133.8**			

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[3] Parks and Kelley, THIS JOURNAL, 47, 2090 (1925).

of the sample. In all cases the pressures are expressed in terms of millimeters of mercury at 0°.

Derived Data

If we neglect the volume of the liquid in the well-known Clausius-Clapeyron relationship and assume the perfect gas equation for the vapor, we obtain the approximation, $\frac{-R\,\mathrm{d}\ln p}{\mathrm{d}(1/T)} = \Delta H$, where ΔH is the heat of vaporization per mole. In the present case the values for $-R \ln p$ were plotted against the reciprocals of the absolute temperatures for both alcohols and the slopes of the two curves were measured at points corresponding to 25 and 50° and the respective boiling points. The values thus obtained for 50° and for the boiling point were then decreased by 1.0 and 4.0%,[4] respectively. The resulting heats of vaporization in calories per mole appear in Table II; they are probably accurate to within 150 calories for the isopropyl alcohol and to within 200 calories for the *tert.*-butyl alcohol. The values at the boiling points compare favorably with the scanty calorimetric data in the literature.[5]

Following Hildebrand,[6] we have also calculated the molal entropy of vaporization (Table II, Col. 5) at the temperature at which the concentration of vapor is 0.00507 mole per liter. As 27.4 cal. per degree is the mean value obtained by Hildebrand for normal liquids, our higher results indicate that these two alcohols are decidedly "polar."

TABLE II

THERMAL VALUES DERIVED FROM THE VAPOR PRESSURE DATA

Alcohol	Heat of vaporization (cal. per mole) At 25°	50°	B. p.	Molal entropy of vaporization (cal. per degree)
*iso*Propyl	10,620	10,490	9,600 (at 82.28°)	33.8 (at 38.7°)
tert.-Butyl	10,890	10,680	9,480 (at 82.86°)	34.4 (at 39.4°)

Summary

1. Vapor pressure measurements have been made on isopropyl alcohol from 0 to 90° and on *tert.*-butyl alcohol from 20 to 90°, inclusive.

2. From these experimental results the heats of vaporization of the two liquids have been estimated for several temperatures. The molal entropies of vaporization indicate that these alcohols are polar liquids.

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[4] These corrections were decided upon after a careful survey of the deviations from the perfect gas law found by Young, Proc. Roy. *Soc.* (Dublin), 12, 376 (1910), for the vapors of alcohols, esters, etc., at corresponding temperatures. The error involved in their use is probably less than 0.5%.

[5] Mathews, THIS JOURNAL, 48, 572 (1926); Landolt-Börnstein-Roth-Scheel, "Tabellen," 1923, p. 1483.

[6] Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, p. 94.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE NATURE OF ACTIVE NITROGEN: THE SYNTHESIS OF AMMONIA FROM THE ELEMENTS[1]

BY BERNARD LEWIS[2]

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The question concerning the nature of glowing active nitrogen has been a much discussed and controversial subject. It is unnecessary here to sketch historically the study of active nitrogen which has led to the atomic and molecular hypotheses of its nature[3] since this has been amply recorded in other works. Birge,[4] Sponer[5] and Birge and Sponer[6] have shown that the eleventh vibrational state of the 9.3-volt electron level, from which the strongest bands in the afterglow proceed, corresponds to 11.4 volts above the normal level and this represents the true energy of combination of nitrogen atoms. This checks with other evidence as discussed by Birge and Sponer[6] as well as with the extrapolated value of the first band in the Lyman-Birge-Hopfield band system formerly attributed to NO by Sponer[4b] but now known to belong to the nitrogen mole-

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[1] Read before the 74th Meeting of the American Chemical Society at Detroit, September 5–10, 1927.

[2] National Research Fellow in Chemistry.

[3] It is very important to make clear the distinction between the atomic and molecular theories with respect to the formation of the afterglow. According to the former, the carriers issuing from the discharge are neutral, unexcited nitrogen atoms which potentially have it within their power to create the glow by means of an activating process involving, as far as our knowledge will allow us to judge, a triple collision between two N atoms and a N_2 molecule. An uncertainty exists regarding the necessity for a triple collision because, unlike the H_2 molecule, the N_2 molecule has definite and known quantized states from which it can radiate, corresponding to the energy of dissociation plus the relative kinetic energy of the atoms. While a three body collision in the ease of the combination of H atoms is an absolute necessity, since there is no molecular quantum state here from which radiation is possible, yet in the N_2 molecule it is possible that two N atoms may combine without the presence of a third body. There are certain difficulties confronting the assumption of a three body collision in active nitrogen (see Bonhoeffer and Kaminsky[8]). It is hoped to treat this in a forthcoming publication. At any rate an excited N_2 molecule results (probably unstable) which gives rise to emission of the afterglow; the a-bands are emitted by transition from vibrational states in level B to several vibration states in level A (see Birge and Sponer[6]), those probably being meta stable. According to the molecular theory the activating process does not occur outside the discharge, since the carriers are held to be metastable excited molecules which originate in the discharge. These have a long life and eventually emit radiation. In the atom theory excitation of metal atoms (Hg, etc.) occurs either by a triple collision with N atoms or by a collision with the resulting excited N_2 molecule. In the molecular theory this excitation takes place directly by collisions with excited N_2 molecules,

[4] (a) Birge, *Nature*, **114**, 642 (1924); (b) **117**, 81 (1926).

[5] Sponer, *Z. Physik*, **34**, 622 (1925).

[6] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

cule.[7] Furthermore, a study[8] of the dependence of the afterglow intensity on the concentration of the active constituent at constant total nitrogen pressure reveals that the relation is bimolecular in character. This and other evidence points strongly to the atom theory. The results of Willey and Rideal,[9] while correct as far as they go, cannot be taken to mean that active nitrogen is composed only of 2-volt excited molecules. These authors neglect to consider many reactions initiated by active nitrogen which require much more energy than 2 volts. The varied phenomena caused by active nitrogen make it evident that 2-volt level nitrogen molecules do not issue from the discharge. It is rather more probable that these vibrational states in the normal electron level, which in all probability are truly metastable, are brought into existence by collisions of the second kind between an ordinary nitrogen molecule and an excited nitrogen molecule in level B. The former takes up from 1 to $3^1/_2$ volts and the latter drops to level A. Vibrating molecules in the normal electron level may also be brought about by a jump from some higher electron level. We can attribute Willey and Rideal's results to molecules in these low vibrational states. In a recent work Constantinides[10] concludes that active nitrogen is an excited molecule having a metastable state between 9.4 and 10.4 volts. This is at variance with our knowledge concerning the origin of the first positive bands as mentioned above. This work will be discussed briefly in a later section.

The importance of determining whether active nitrogen contains atomic nitrogen is evident. The present experiments were undertaken with this in mind and they probably furnish the first kinetic evidence of its kind that nitrogen atoms are present in active nitrogen. In principle the experiments depend upon the formation of ammonia from the elements. It is easily shown that if unactivated nitrogen gas is mixed with atomic hydrogen (prepared by Wood's method), at least four successive and selective collisions passing through intermediate unstable compounds are necessary in order to form ammonia. The following set of equations is not intended to indicate the order of the steps involved nor the possibility of their occurrence, only that such a sequence is required to reach the final product.

$$N_2 + H = N_2H \tag{1}$$

$$N_2H + H = N_2H_2 \tag{2}$$

$$N_2H_2 + H_2 = N_2H_4 \tag{3}$$

$$N_2H_4 + H_2 = N_2H_6 \longrightarrow 2NH_3 \tag{4}$$

If the gases are brought together at low pressures the chance is very small that the entire series will be completed especially in view of the

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[7] Sponer, Z. *Physik*, 41,611 (1927).

[8] Bonhoeffer and Kaminsky, *Z. physik. Chem.*, 127,385 (1927).

[9] Willey and Rideal, J. *Chem. Soc.*, *1804*, 1926; 669, 1927.

[10] Constantinides, *Phys. Rev.*, 30, *95* (1927).

rarity of such encounters as depicted by Equation 2. Similarly it can be shown that on bringing together unactivated hydrogen and active nitrogen three or four successive and selective encounters are required, depending on whether the series commences with molecular or atomic nitrogen. In both of these types of experiments the chance for forming ammonia should be very slight. If now atomic hydrogen is mixed with active nitrogen there are two possibilities; with the metastable nitrogen molecule the sequence is composed of four steps similar to that given above; on the other hand if atomic nitrogen is present, only two steps are necessary, neither of them being of rare occurrence, since Wood's hydrogen contains a considerable amount of atomic hydrogen.

$$N + H = NH \quad (1)$$
$$NH + H_2 = NH_3 \quad (2)$$

Thus the synthesis of ammonia has the best chance of occurring, if at all, only when both gases are activated and provided the activated nitrogen contains atomic nitrogen. The alternative to such a series of steps would necessitate a triple, quadruple or quintuple collision which would still place the last-mentioned possibility in the most favorable position for ammonia formation. Of course, the presence of neutral, tri-atomic hydrogen might form ammonia in a single step, but its existence is extremely doubtful.[11]

There is one other possibility to be considered, namely, the following reaction with excited nitrogen molecules.

$$N_2' + H = NH + N \quad (1)$$
$$NH + H_2 = NH_3 \quad (2)$$

If this were taking place Caress and Rideal[12] would have observed ammonia formation in the gas phase at potentials corresponding to the numerous vibrational states in the 7.9-volt and 9.3-volt electron levels in the nitrogen molecule. Instead they found ammonia formation beginning at 13 volts, which they represented as a series of steps commencing with ordinary nitrogen and an excited H'_{13v}. Since their electron tube was not calibrated and a tungsten filament was employed, this voltage may be in error by at least one volt. While the hydrogen atom has critical potentials from 10.2 volts and up, it is strange why, if their mechanism is correct, ammonia is not formed in the gas phase at 10.2 volts, the first resonance potential of the hydrogen atom. Now this is very significant in view of the fact that level C (see Birge and Sponer[6]) of the nitrogen molecule begins at 13 volts and that the vibrational states of level B beginning at 9.3

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[11] (a) Paneth, Klever and Peters, Z. *Elektrochem.*, 33, 102 (1927); (b) Urey and Smallwood, unpublished material; (c) Bach, *Ber.*, 58B, 1388 (1925); (d) Scanavy-Grigoriewa, Z. *anorg. allgem. Chem.*, 159, 55 (1927); (e) Artius, *Dissertation*, Heidelberg, *1926;* (f) Fischer and Iliovici, *Ber.*, 41, 4452 (1908).

[12] Caress and Rideal, *Proc. Roy. Soc. (London),* 115, 684 (1927).

volts extend up to about 12.8 volts. It is well known that in contradistinction to iodine and oxygen molecules, the nitrogen molecule does not dissociate in a primary act. According to Birge and Sponer in the case of certain excited electronic states (such as level B in nitrogen) dissociation does not take place when the energy of dissociation is reached even with collisions occurring. Assuming that one product of dissociation is an excited atom, their predicted break in the series of vibrational states to account for this is observed in C level, $n = 4$ at 13.94 volts. This may correspond to a collisional dissociation of the molecule into a normal nitrogen atom and a 2.5-volt excited N atom, which is possible from certain findings by Hopfield.[13] This is in agreement with conclusions derived from the extrapolated convergence limit of the upper band of the Lyman-Birge-Hopfield band system.' Thus Caress and Rideal's observed reaction in the gas phase at 13 volts ± 1 volt may, in the light of the foregoing, be represented more logically by excitation of the nitrogen molecule above its dissociation energy (probably to some vibrational state in the C level), followed by collisional dissociation into atoms. Ammonia is then easily formed through the medium of atoms as represented in a mechanism above.

Experimental

The electrodeless discharge for preparing active nitrogen, employed by other workers with excellent results, was substituted for the usual condensed discharge with internal electrodes, since the gas pressure was low. The experimental arrangement is shown in Fig. 1. The active nitrogen was prepared in a spherical bulb A (12.7 or 8.7 cm. in diameter) wound with a few turns of heavy copper wire. The electrical connections are evident. **A** zinc spark-gap was employed and the plate-glass lead foil condenser (5 in number, 18 X 20 inches) was immersed in transformer oil. The transformer primary was supplied with 9 to 10 amperes at 110 volts, 60 cycles, and the secondary voltage was about 20,000 volts. At a well-defined pressure (about 0.1 mm. in the 12.7 cm. and about 0.05 mm. in the 8.7 cm. bulb) a brilliant ring discharge appeared from which glowing active nitrogen was drawn and under good conditions could be observed to last between one and two minutes. Tank nitrogen was passed over heated copper to remove most of the oxygen, through soda lime and phosphorus pentoxide tubes and then through a liquid air trap L, nearly atmospheric pressure being maintained by a mercury trap M. By means of a needle valve V, the pressure in **A** could easily be regulated at any desired value. Atomic hydrogen was prepared in a Wood's discharge tube B, 2 meters long and 2 cm. in diameter with cylindrical aluminum electrodes. The transformer primary was supplied with from 10–14.5 amperes at 110 volts, 60 cycles, and the secondary voltage was about 20,000 volts. The atomic hydrogen, whose presence could be shown by a glowing platinum strip, was drawn from the center of the discharge tube where the brilliant spectrum due to the Balmer series was always in evidence. The hydrogen was prepared from a potassium hydroxide solution in a long armed U-tube continuous generator G, care being taken to prevent the oxygen from mixing with the hydrogen by allowing the platinum electrodes to just touch the liquid surface in each arm. Any caustic in the gas was carefully removed. The pressure was regulated as

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[13] Hopfield, Phys. *Rev.*, 27, 801 (1926).

before by means of a needle valve. A calibrated McLeod gage was connected to both the nitrogen and hydrogen systems just before each gas entered its respective discharge tube. The entire apparatus with the exception of the needle valves was constructed of Pyrex glass. The gases, after leaving the discharge, were brought together in a chamber C, the hydrogen through a 1mm. nozzle about 24 cm. from its discharge tube and the nitrogen through a 2mm. stopcock about 20 cm. from the electrodeless discharge. The tubes leading from both discharges were grounded in several places with tin-foil to eliminate as far as possible stray high-frequency currents. Both transformers were at some distance from the discharges. A little excess pressure could be maintained on the hydrogen side. With due precaution exercised in starting an experiment, it was found that no mixing of the gases occurred outside the mixing chamber during the progress of a run. Any diffusion and mixing of the gases in either is immediately noticeable by suppression of the Balmer lines in the hydrogen tube and the appearance of a pinkish color instead of the usual greenish-yellow in the nitrogen discharge. All three types of experiments were carried out under the same conditions. Condensable gases were frozen out in a ground-glass jointed liquid-air trap D, the gases being pulled through the system by two high-vacuum oil pumps joined in parallel. At the close of an experiment the trap was removed, distilled water added while still in liquid air and the tube stoppered. Tests for ammonia were made with freshly prepared Nessler reagent and for hydrazine with selenious acid and silver nitrate, the hydrazine first having been stabilized with a drop of sulfuric acid. With selenious acid a reddish precipitate develops and with silver nitrate silver precipitates. Blank tests were made in every case with distilled water.

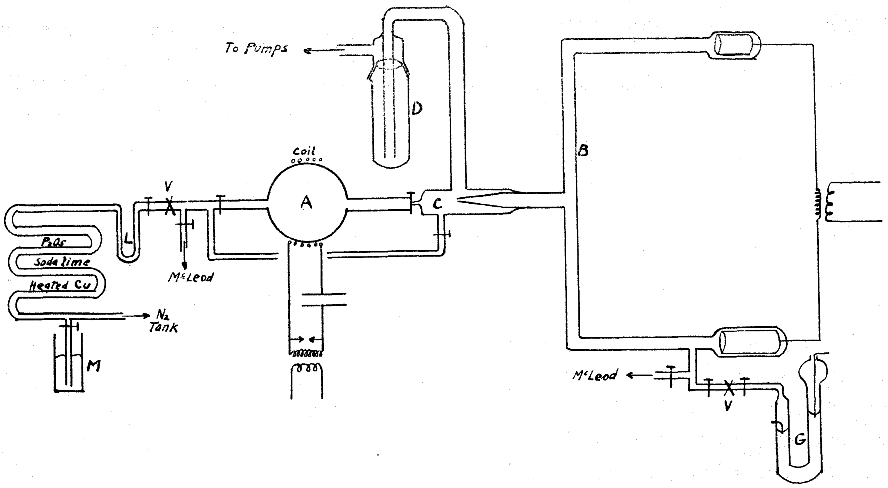

Fig. 1.

Results

The following table presents the results of a series of runs.

The results show that *ammonia is formed only when active nitrogen is mixed with atomic hydrogen.* From considerations presented above, this can be interpreted to indicate the presence of nitrogen atoms in active nitrogen.

TABLE I

RESULTS OF A SERIES OF RUNS

Press., mm. of Hg N_2	H_2	Gas activated	Time of run, min.	Result and remarks
0.15	0.26	H_2	30	No NH_3. After one day no difference between test solution and blank test
.31	.42	H_2	60	No NH_3
.25	.375	H_2	60	No NH_3; no N_2H_4
.33	.38	H_2	85	No NH_3; no N_2H_4
.17	.28	H_2	60	No NH_3; no N_2H_4
.04	.10	H_2	60	No NH_3; no N_2H_4
.09	.15	N_2 and H_2	60	NH_3 present, deep yellowish-red characteristic color with $^1/_3$ of solution. No N_2H_4
.076	.076	N_2 and H_2	90	NH_3 present, deep characteristic color with $^1/_3$ solution. No N_2H_4
.04	.044	N_2 and H_2	85	NH_3 present; deep yellow color with tinge of red with $^1/_2$ of solution. No N_2H_4
.25	.39	Blank run, no activation	60	No NH_3; no N_2H_4
.045	.045	N_2	60	No NH_3; no N_2H_4
.047	.040	N_2	50	No NH_3; no N_2H_4

Discussion

To the author's knowledge this is the first attempt to bring together active nitrogen and atomic hydrogen after the activation of each gas separately. Previously either nitrogen or hydrogen alone or a mixture of the two gases was activated. The results of these experiments activating the nitrogen only are in agreement with those of other investigations.[14,9] *Active nitrogen has no effect on molecular hydrogen, no ammonia being formed.* The evidence for the formation of ammonia upon mixing ordinary nitrogen with atomic hydrogen is conflicting. Hirst[15] found ammonia and traces of hydrazine when hydrogen in the presence of nitrogen was activated by collision with optically excited mercury atoms. This may have been due to the presence of a mercury surface, which agrees with the observations of Caress and Rideal[12] on the formation of ammonia on a metal surface with hydrogen atoms and nitrogen molecules. At pressures above but not below atmospheric, W. A. Noyes, Jr.,[16] obtained ammonia at the temperature of boiling mercury by a similar method of hydrogen activation. On the other hand, H. S. Taylor,[17] employing the same means for excitation failed to detect any ammonia. Bon-

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[14] Strutt, Proc. Roy. *Soc. (London)*, 85, 219 (1911).

[15] Hirst, *Proc. Camb. Phil. Soc.*, 23, 162 (1926).

[16] W. A. Noyes, Jr., THIS JOURNAL, 47, 1003 (1925).

[17] (a) Taylor, Trans. Faraday *Soc.*, 21, 562 (1926); (b) THIS JOURNAL, 48, 2840 (1926).

hoeffer[18] also failed to find ammonia using the Wood's discharge tube for producing atomic hydrogen. Cario and Franck[19] also obtained negative results with atomic hydrogen and molecular nitrogen. Willey and Rideal[20] state that they were able to obtain ammonia when a stream of nitrogen at 10 mm. pressure was led into a stream of hydrogen at a point 150 cm. (corrected by Dr. Willey) from a discharge tube through which hydrogen was flowing at the same pressure. The gas pressure was far too high for the preservation of atomic hydrogen 150 cm. from the discharge.[21] In Willey and Rideal's experiment the presence at the mixing point of any form of ionic hydrogen or an electronically excited atom is precluded and, since the existence of H_3 is problematic, it is a little difficult to understand what variety of active hydrogen they were dealing with. It may be concluded from the present results and other evidence available that *no ammonia is formed by atomic hydrogen and unexcited molecular nitrogen.*

In support of the present results on the formation of ammonia when both hydrogen and nitrogen were activated separately may be cited the experiments of Andersen[22] and Storch and Olsen[23] on the formation of ammonia from gaseous mixtures of nitrogen and hydrogen with slow electrons and in the low-voltage arc. Olsen[24] concludes that the main synthesis of ammonia is brought about by the presence of both normal nitrogen atoms and normal hydrogen atoms.

Brief mention should be made of Constantinides' experiments.[10] If the effects observed by him represent ionization, then it would appear that active nitrogen is able to ionize iodine but not mercury (ionization potentials, 9.4 volts and 10.4 volts, respectively). From this it was concluded "that active nitrogen is an excited molecule of nitrogen having a metastable state between 9.4 and 10.4 volts." This does not eliminate the atom theory as it would at first appear. Our knowledge of energy transfer in triple collisions is still obscure. Physical intuition would indicate that all the energy of combination of nitrogen atoms might not be transferred to systems like iodine or mercury, expecially in view of the known low vibration states in the normal electron level in the nitrogen molecule. This would be equally true whether these systems collided directly with two nitrogen atoms or with an excited nitrogen molecule. Furthermore, it is unreasonable to assume that a symmetrical collision between two nitrogen atoms and a nitrogen molecule would in-

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[18] Bonhoeffer, *Z. physik. Chem.*, 119, 385 (1926).

[19] Cario and Franck, *Z. Physik,* 37, 619 (1926).

[20] Willey and Rideal, *J. Chem. Soc.*, 671, 1927.

[21] Compare Kaplan, *Phys. Rev.*, 30, 640 (1927).

[22] Andersen, *Z. Physik,* 10, 54 (1922).

[23] Storch and Olsen, This Journal, 45, 1605 (1923).

[24] Olsen, *ibid.*, 48, 1298 (1926).

volve the same energy transfer as a collision between two nitrogen atoms and iodine or mercury. This argument is very significant if the combination of nitrogen atoms involves a two body collision only. It is not at all surprising, therefore, to find that active nitrogen is incapable of transferring 10.4 volts to mercury. Active nitrogen even seems to be incapable of producing an active variety of hydrogen,[20] the dissociation of which requires only 4.2 volts. One prediction may possibly be allowable. The higher the nitrogen pressure the more readily are the α bands eliminated due to secondary collisions in which the excited nitrogen molecules are divested of small amounts of energy. This is borne out by observations on the afterglow decay time and intensity with increasing nitrogen pressure. At low pressures, therefore, active nitrogen may be expected to transfer more energy to mercury. Indeed, Ruark, Foote, Rudnick and Chenault,[25] by recording the emission of the mercury $2^3P_1 - 6^3D$ series at 0.02 mm. nitrogen pressure, showed that at least 10 volts could be transferred to mercury. It is possible that at this and lower pressures some mercury atoms may be ionized.

Conclusion

It may be concluded from these experiments that active nitrogen contains atomic nitrogen. Until the atomic origin of active nitrogen is shown definitely to be erroneous, this can be taken as supporting the present interpretation of spectroscopic data. Since the nitrogen molecule may exist in many states of excitation, it is evident that at any moment glowing active nitrogen would consist of a non-homogeneous mixture of normal nitrogen atoms and nitrogen molecules in a number of excited states. An intimation that active nitrogen contains more than one active constituent may be gathered from a conclusion of Lord Rayleigh (Strutt)[26] that "there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress." Since this paper was originally written, a private communication from Dr. a. J. B. Willey and later his letter to *Nature*,[27] also a suggestion by Bonhoeffer and Kaminsky,[8] indicate that these workers also suspect the non-homogeneity of active nitrogen.

Summary

Experiments are described for determining whether atomic nitrogen is a constituent of glowing "active nitrogen." The latter, prepared at low pressures by an electrodeless discharge, was passed into a stream of atomic (Wood's) hydrogen. The resulting mixture yielded ammonia. Under the same conditions no ammonia was obtained when either the

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[25] Ruark, Foote, Rudnick and Chenault, *J. Optical Soc. Am.*, 14, 17 (1927).

[26] Strutt, *Proc. Roy. Soc. (London)*, 88, 549 (1913).

[27] Willey, *Nature*, 119, 924 (1927).

nitrogen or hydrogen was activated alone. No hydrazine was found under any conditions. Considerations are presented showing that at low pressures ammonia would be expected, if at all, only when both the nitrogen and hydrogen are activated simultaneously and provided atomic nitrogen were present in the former. It is concluded that active nitrogen contains atomic nitrogen, which may be taken as support for the present interpretation of spectroscopic data. In addition it is concluded that glowing active nitrogen consists of a non-homogeneous mixture of nitrogen atoms and excited nitrogen molecules.

MINNEAPOLIS, MINNESOTA

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

THE SYSTEM WATER AND THE SULFATES OF SODIUM AND MAGNESIUM[1]

BY WALTER C. BLASDALE AND HOMER L. ROBSON

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In 1915 D'Ans[2] summarized the work of van't Hoff,[3] Roozeboom[4] and others on this system, and made sufficient new determinations to indicate the equilibrium relations in this system between 0 and 90°. The isotherm at 25° was determined by W. C. Blasdale in 1920 in connection with a study of the salt pair, sodium chloride--magnesium sulfate,[5] and the isotherm at 103° was similarly determined by Mayeda[6] in the same year. Archibald and Gale[7] in 1924 determined isotherms of this system at 0°, 10°, 18.7°, 25°, 30°, 40°, 50°, 60°, 80° and 100°, combining new determinations with the results of previous investigators. Their isotherms below 60° are in very fair agreement with those given by D'Ans, but those at 80 and 100" differ considerably. Mayeda's measurements disagree with those of D'Ans and of Archibald and-Gale and are somewhat different from the values given in this paper.

The salts which occur below 60° are: the dodecahydrate, heptahydrate and hexahydrate of magnesium sulfate; sodium sulfate, decahydrate and

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[1] A part of this work was done under a grant made by the University of Saskatchewan from its research fund.

[2] D'Ans, *Kali*, 9, 177 (1915).

[3] Van't Hoff, *Rec. trav. chim.*, 6, 36 (1887); (b) van't Hoff and van Deventer, *Z. physik. Chem.*, 1, 170 (1887); (c) van't Hoff and Meyerhoffer, *Sitzb. preuss. Akad. Wiss.*. Berlin, 1904, p. 1418; (d) van't Hoff, "Untersuchungen über der Bildungsverhaltnisse der Ozeanischen Salzablagerungen," 1912 ed., p. 281; (e) van't Hoff and O'Farrelly, *Sitzb. preuss. Akad. Wiss.*, Berlin, 1902, p. 370; (f) "Untersuchungen," p. 198.

[4] (a) Roozeboom, *Rec. trav. chim.*, *6*, 333 (1887); (b) Roozeboom, *Z. physik. Chem.*. 2, 513 (1888).

[5] Blasdale, *J. Ind. Eng. Chem.*, 12, 164 (1920).

[6] Mayeda, *J. Chem. Ind.* (*Japan*), *23*, 573 (1920).

[7] Archibald and Gale, THIS JOURNAL, 46, 1760 (1924).

anhydrous; and the double salt, astrakanite ($MgSO_4.Na_2SO_4.4H_2O$). We have found that these salts come to equilibrium with their aqueous solutions with reasonable rapidity. Above 60° loweite ($MgSO_4.Na_2SO_4.$-$2/5H_2O$), vanthoffite ($MgSO_4.3Na_2SO_4$) and kieserite ($MgSO_4.H_2O$) occur. These salts come to equilibrium much more slowly and easily form supersaturated solutions. This is probably the cause of the disagreement of previous workers in this region.

We have made equilibrium measurements between **67** and 100°, including a determination of the isotherm at 75, 85, 95 and 100°, and have made sufficient measurements between 100 and 210° to indicate roughly the equilibrium relations within this temperature range. These measurements have been carefully compared with those of previous investigators and isotherms have been constructed for all temperatures for which data were available. Fig. 1 has been constructed from the isotherms as described below. From this figure the composition of any stable solution in this system may be found for the temperature interval 0 to 210°.

The heavy lines in Fig. 1 represent univariant systems and form a figure similar to that employed by D'Ans. They give the composition of solutions in equilibrium with two solid phases; the points which they intersect give the composition of invariant solutions. Temperature is measured on the horizontal axis and the composition of the solution on two vertical axes, one extending above and one below the heavy horizontal line. The upper vertical axis gives the magnesium sulfate concentration of the solution in grams of magnesium sulfate per 100 g. of water, and the lower gives the concentration of sodium sulfate similarly expressed; therefore the magnesium sulfate concentration of any univariant solution may be found from the line representing it in the upper part of the diagram and the sodium sulfate concentration from the corresponding line in the lower part. The circles represent equilibrium measurements given in Table II.

The fine lines give the total concentration of salts in grams per 100 g. of water. From them the composition of any solution in equilibrium with a single salt may be determined. Thus, to find the sodium sulfate concentration of a solution in equilibrium with astrakanite at 45°, which contains **46** g. of magnesium sulfate per 100 g. of water, the point in the upper part of the diagram corresponding to 46 g. of magnesium sulfate at 45° would be found. This lies between the fine lines representing total salt concentrations of **56** and 57 g. per 100 g. of water, and a value of **56.7** is obtained **by** interpolation. As **46** g. of this is due to magnesium sulfate, the remaining 10.7 grams would be the concentration of sodium sulfate in the solution. In this manner isotherms can be constructed from this diagram for any temperature between 0 and 210°.

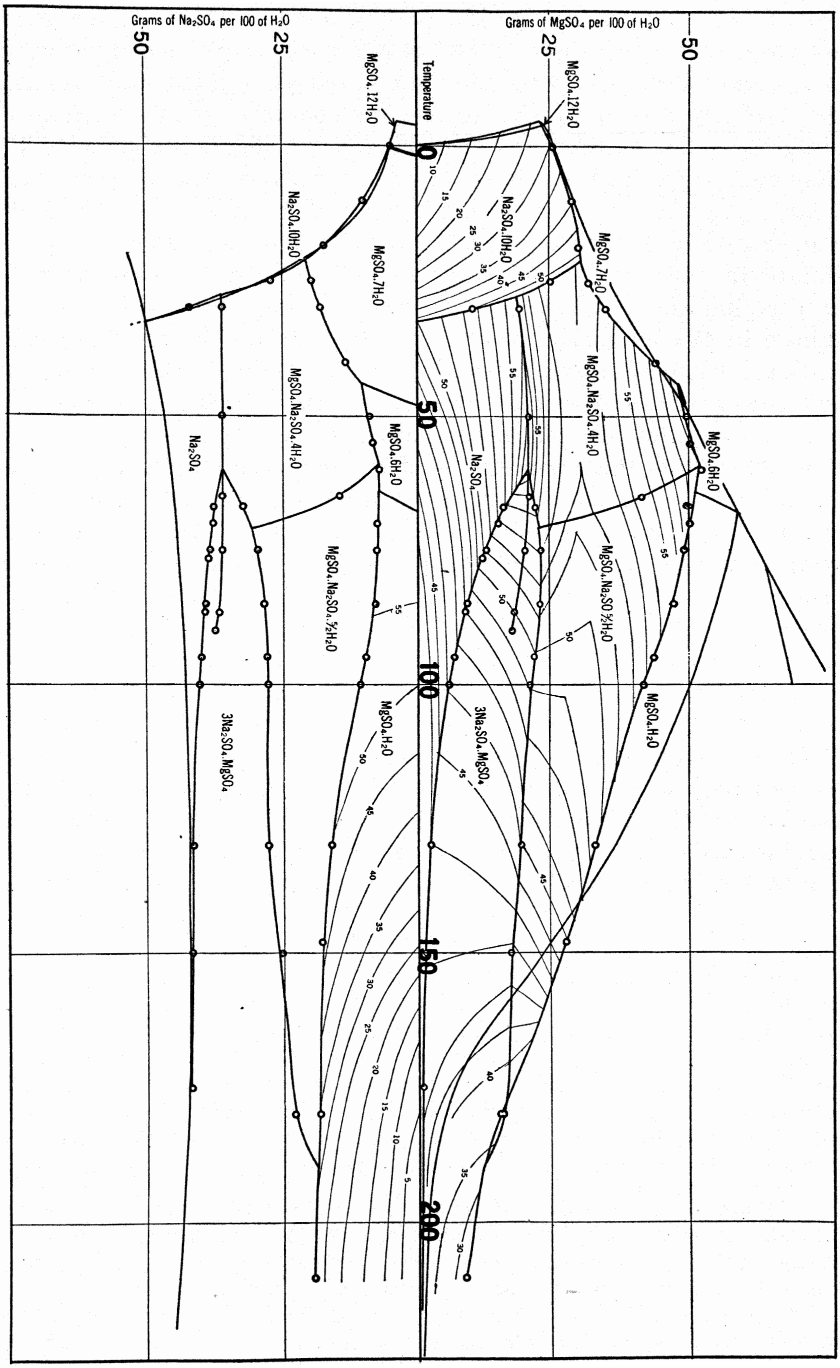

Fig. 1.—The system between —5 and 210°.

In attempting to correlate the data of previous observers it was found advantageous to eliminate the water as a variable and to plot the per cent. of magnesium sulfate in the total anhydrous salts in the solutions against the temperature, according to the method of Jänecke.[8] Data which disagreed when plotted as isotherms or on a diagram similar to Fig. 1 frequently agreed reasonably well when plotted on this type of diagram, a large part of the discrepancies being due to an error in the total salt concentration rather than in the ratio of magnesium sulfate to sodium sulfate in the solution. Smooth curves were drawn through the data on this diagram and these gave the ratio of magnesium sulfate to sodium sulfate in the univariant solutions. The data on the total salt concentration for each univariant system were then plotted against temperature and smooth lines drawn through the points, which met corresponding lines representing other univariant systems at the invariant points. From these two plots the compositions of the univariant systems were determined and plotted as the heavy lines of Fig. 1. Next, series of isotherms at intervals of 5 and 10° were made, based on the data for the univariant systems which had been determined as above described. The published measurements of Roozeboom and of Archibald and Gale and those which we determined were plotted on these isotherms and smooth lines drawn through the points. From the data given by these, the fine lines in Fig. 1 were constructed, alterations in the isotherms being made where necessary to avoid improbable distortion of the fine lines. The fine lines were placed at intervals of 5 g. of total salts per 100 g. of water in the areas representing solutions in equilibrium with sodium sulfate decahydrate and kieserite, as the diagram would be unduly complicated by placing them at unit intervals. Unit intervals are employed for the areas representing astrakanite, loweite, vanthoffite and thenardite (anhydrous sodium sulfate).

Preparation of Salts

Commercially obtainable epsomite ($MgSO_4.7H_2O$), mirabilite ($Na_2SO_4.10H_2O$) and thenardite were employed for these salts and their filtered solutions for the preparation of the others. Magnesium sulfate hexahydrate is easily prepared by the evaporation of a solution of magnesium sulfate between 50 and 75°. Astrakanite was prepared by evaporating equimolecular solutions of the component salts at 50–55° and good crystals up to 1 cm. in length were grown from solutions at 60–95°. We did not succeed in growing single crystals at temperatures below 50° which were suitable for goniometer measurements.[9] Löweite was prepared by the slow evaporation of a

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[8] Janecke, *Z. anorg. Chem.*, *51*, 132 (1906). This method has been described by Blasdale, "Equilibrium in Saturated Salt Solutions," A. C. S. Monograph Series, 1927, employing this system as an example. The diagram there given does not include the results of our measurements, which were unfinished at the time of writing.

[9] For data on the crystallography of astrakanite, see von Jeremejeff, *Z. Kryst.*, 23, 269 (1891). In the literature this salt is also referred to as bloedite and as simyonite, see Jaeger, *Tschermaks' Min. Pet. Mitt.*, 22, 102 (1903).

solution containing magnesium and sodium sulfates in the molecular ratio of 3:2 at the boiling point, with additions of an equimolecular solution from time to time to maintain a constant composition of the solution. The precipitated salt was centrifuged and then pressed between filter paper while still warm. Each batch was analyzed and found to contain very little excess magnesium sulfate and nearly the theoretical water. A small amount of astrakanite was detected by microscopic examination. The presence of this small amount of astrakanite ordinarily does not matter and it can be removed by drying the salt in a partly closed vessel at 110° when necessary.

Vanthoffite was prepared by the slow evaporation of its congruent solution close to the boiling point, the solution being well seeded and vigorously agitated with a stream of compressed air. The salt was centrifuged and dried at 110°. It is very difficult to prepare this salt at temperatures below 95° as thenardite and astrakanite form more readily than the stable vanthoffite.

Kieserite was prepared by drying epsomite in air as described in a previous paper" and by stirring solutions of magnesium sulfate in contact with seed at 80–100°. The latter method gives a product which is very difficult to dry and is best stored wet at a temperature above 70°.

Identification of Compounds

The solid phases in contact with the analyzed solutions were identified by analysis and by their optical properties, which are in Table I.[11]

TABLE I

OPTICAL PROPERTIES OP THE SALTS

Salt	a	β	γ	2V	Sign	Disp.	Orientation	System
Hexahydrate	1.438	1.463	1.465	29"	−	$\rho > v$	Y = b, $X_\wedge c$ −25"	Mono.
Kieserite	1.523	1.525	1.596	57"	+	$\rho > v$	Y = b, $Z_\wedge c$ 76.5°	Mono.
Thenardite	1.464	1.474	1.485	84°	+	$\rho > v$(w)	X = b, Y = c	Ortho
Vanthoffite	1.485	1.488	1.489	84°?	−	$\rho < v$	....	Mono.?
Astrakanite	1.486	1.488	1.489	71°	−	$\rho < v$(str.)	Y = b, $X_\wedge c$ 41.1"	Mono.
Löweite	...	1.471	1.490	Uni-axial	−	...	....	Rhombo-hedral

Löweite is easily recognized by its uniaxial interference figure, hexahydrate by its figure and low index of refraction, and kieserite by its fine-grained structure and high index. Vanthoffite and astrakanite were difficult to distinguish and closely resemble thenardite from which they may be distinguished by their lower birefringence. The crystal form and optical orientation were frequently made use of. Many of the crushed fragments of thenardite have a diamond-shaped appearance, with an angle close to 60° (theor. 61° 44' for $110_\wedge 1\bar{1}0$); vanthoffite forms some diamond-shaped crystals with a much sharper angle. Astrakanite occurs in laths and in combinations of the base, unit prism and dome (001, 110 and 101). The presence of vanthoffite, astrakanite and thenardite was verified by analysis or by means of a check on the salts added.

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[10] Robson, THIS JOURNAL, 49, 2772 (1927).

[11] Larsen, "The Microscopic Identification of the Non-Opaque Minerals," Bulletin 679, U. S. Geological Survey, 1921. The data for magnesium sulfate hexahydrate are those given by Robson, ref. 10.

In examining the optical properties of the various solid phases a small portion was removed, rubbed dry on warmed blotting paper and examined with a petrographic microscope employing suitable immersion media. When an analysis of the solid phase was required, 2–5 g. was removed from the solution and quickly dried with filter paper, weighed, made up to volume and analyzed. No attempt was made to employ the residue method of Schreinemakers.[12]

The presence of astrakanite in samples known to contain thenardite or loweite, and of vanthoffite in samples containing thenardite or loweite, was determined from the ratio of magnesium sulfate to water in the sample. All doubtful analyses were rejected. Vanthoffite and astrakanite would not occur together except along the univariant line between 60 and 71°.

In making many of the measurements the solid phases were first prepared and analyzed, weighed amounts added to the solubility tubes and a solution of the expected equilibrium concentration, prepared by the evaporation of standardized stock solutions of the two sulfates to a definite strength, was added, The volume was noted before and after stirring. Any alteration in the solid phases would have been readily detected by comparing the analysis of the final solution with the known amount of water and salts added to the tubes.

The optical examination of the solid phases greatly facilitated the preliminary work and gave positive identification in cases where other methods alone would have left some room for doubt.

Transition Points

The transition point of magnesium sulfate dodecahydrate and heptahydrate was determined by Cottrel[13] to be 1.8' and the cryohydric point, dodecahydrate-ice-solution of magnesium sulfate, to be —3.9°. We assume that the corresponding point, dodecahydrate-mirabilite-ice-solution of sodium and magnesium sulfates, will be about —5° and the invariant point, dodecahydrate-mirabilite-epsomite-solution of sodium and magnesium sulfates, about 0°. The invariant point, epsomite-mirabilite-astrakanite-solution, was determined by van't Hoff[1c] thermometrically to be 20.6° and the invariant point, mirabilite-astrakanite-thenardite-solution, thermometrically by D'Ans[2] as 27°. The transition of epsomite to hexahydrate was found to occur at 48.4° by Carpenter and Jette,[14] and this temperature is probably lowered 4° by the presence of astrakanite. We determined the invariant point, hexahydrate-astrakanite-löweite-solution, dilatometrically, to be about 59.5'. Two tubes were employed, the first giving a contraction below 58.5' and an expansion above 60.5°, and

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[12] Blasdale, ref. 8, page 86.

[13] Mentioned by van't Hoff, Meyerhoffer and Smith, *Sitzb. preuss. Akad. Wiss.*, Berlin, 1901, p. 1035; "Untersuchungen," p. 173.

[14] Carpenter and Jette, THIS JOURNAL, 45, 578 (1923).

the second a contraction at 59° and an expansion at 60.2°. The invariant point, astrakanite-vanthoffite-thenardite-solution was found to be 60° by interpolation as the equilibrium was established so slowly it was not possible readily to determine the point by dilatometric or tensimetric methods. Van't Hoff, Meyerhoffer and Smith[13] found the transition of hexahydrate to kieserite to occur at 68° in contact with a solution of magnesium sulfate; the presence of loweite would probably lower this temperature by 4°. The invariant point, astrakanite-löweite-vanthoffite-solution, was found by van't Hoff and O'Farrelly[3e] to lie at 71° by dilatometric investigation.

The transition of loweite to vanthoffite and kieserite occurs above 100°. Jänecke[15] obtained seemingly conclusive evidence for a transition temperature between 120 and 130° with a strong expansion accompanying the transition. We were unable to verify his findings. Two Pyrex dilatometers, the lower portion of one of which is represented in Fig. 2, were employed, with balancing columns of mercury three meters high in a tube 0.8 mm. in diameter and a bulb of 60 cc. capacity. With these the region between 115 and 137° was explored very carefully and no expansion was observed. The tubes were loaded with finely powdered kieserite, loweite and vanthoffite, with about 10% of astrakanite to provide the proper solution on melting at 71°. These were exhausted rapidly at 80°, filled with paraffin oil (Nujol) and sealed off; after filling the arm with mercury they were brought to equilibrium at 115 and 120°, respectively. A slow contraction accompanied the conversion of the kieserite in the charge to loweite, and this was completed in three days at 120°. At the conclusion of the trial with the second dilatometer, which lasted three weeks, the bath was brought to 120° and the dilatometer gave the initial reading. The room temperature was kept within one degree of 22° for one half hour preceding measurements to avoid any effect of temperature on the mercury column. An expansion corresponding to the initial contraction could have been easily observed without this precaution.

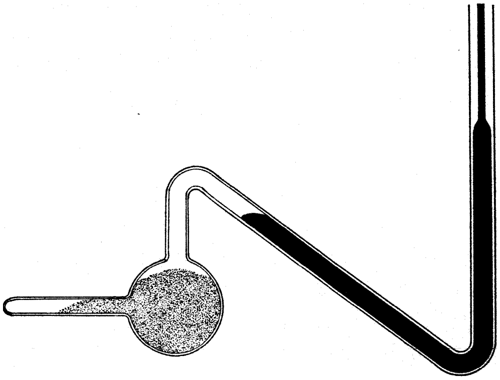

Fig. 2.—Cross section of lower portion of tensimeter.

This type of apparatus became awkward for making **observations** at higher temperatures than 137°, so experiments were continued employing

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[15] Jänecke, *Kali*, 11, 12 (1917).

the solubility bomb described below. The bomb was charged with a saturated equimolecular sodium and magnesium sulfate solution and loweite, with a small amount of kieserite and vanthoffite as seed, and stirred at the required temperature for one or two days. At the conclusion of stirring the solution was drained from the solid phase by inverting the bomb and opening the valve until all the liquid had passed out; the bomb was then quickly opened and the solid phase examined with the petrographic microscope. Löweite was clearly detected in all mixtures stirred, up to 180°, but was replaced by vanthoffite and kieserite at 210°. The exact transition point, representing the equilibrium

$$3MgSO_4.Na_2SO_4.5/2H_2O \longrightarrow MgSO_4.3Na_2SO_4 + 2MgSO_4.H_2O + \text{solution}$$

was not determined, but probably lies close to 190°.

Solubility Determination

The equilibrium determinations below the boiling point were made by stirring the mixtures of salt and water in tubes of Pyrex glass 4 cm. X 30 cm. with a screw stirrer 10 cm. long and 2.5 cm. wide. The stem of the stirrer was 0.8 cm. thick and 30 cm. long, and rotated in a Pyrex tube which passed through two close-fitting rubber stoppers, one at the top of the tube and one below the level of the oil in the bath. This arrangement prevented water from distilling out of the tube or condensing on the cooler portions inside it. Individual motor drives were found to be more satisfactory than a main pulley drive. A load of 150 g. of solution and 100 g. of salts was usually charged.

In the preliminary experiments the stirrers were driven at 150 r. p. m. With this speed of stirring, equilibrium was attained very slowly and in some cases variable results were obtained after several weeks of stirring. With a stirring speed of 1000 to 1500 r. p. m. equilibrium was attained much more rapidly. We did not observe any shift in the equilibrium with variation in the speed of stirring. Some experiments were made in which the proper amounts of thenardite and epsomite were added in lieu of vanthoffite and loweite, but the solutions obtained were supersaturated unless stirred for an impractical length of time.

The experiments above 100° were made with an apparatus similar to one already described,[10] except that a different head was made for the bomb. The diagram of the head is given in Fig. **3.** The nipple of the condenser is fastened into the head by a threaded sleeve. The opening into which this fits is closed by a plug during stirring. The solution on passing the filter and needle valve had only to travel through 15 mm. before entering the nipple of the condenser, which is 3 mm. wide and 40 mm. long. This is attached to the main condenser tube, which is 10 mm. wide and 50 cm. long, the last 30 cm. being bent in the form of a U-tube, which was immersed in ice water during sampling. This arrangement has been employed in working with solutions of potassium chloride and sulfate and has proven very satisfactory. Different filter disks (Alundum disks, mix R. A. 225, supplied by the Norton Co.) from those employed for the system magnesium sulfate-water were employed and these let a small amount of very finely-divided kieserite through, giving the mixtures a milky appearance. Only one-third by weight of the charge was solution, to avoid any possibility of supersaturation. The exact amount of error from the kieserite passing the filter was not determined, but measurements of the solubility of magnesium sulfate alone under similar conditions gave results very little above the known curve and the error is probably less than 2 g. of magnesium sulfate per 100 g. of water. Preliminary measurements showed that the solutions did not come to equilibrium between 100 and 175° very much faster than between 75 and 100°.

Solutions supersaturated with respect to vanthoffite were prepared by evaporating appropriate mixtures of the stock solutions of the two sulfates. These precipitated astrakanite spontaneously and came to equilibrium in two or three hours. If seeded with about 2% of vanthoffite and stirred rapidly, stable equilibrium was obtained in one or two days. Solutions supersaturated with respect to löweite came to equilibrium with it most rapidly when the ratio of sodium sulfate to magnesium sulfate approached that required for equilibrium with vanthoffite; those with a higher ratio of magnesium sulfate to sodium sulfate required one or two days' stirring before reaching equilibrium. Solutions containing up to 50% more magnesium sulfate than that required for equilibrium with kieserite were easily prepared by evaporation. These required four to six days' stirring in contact with 10–20% of seed to come to equilibrium.

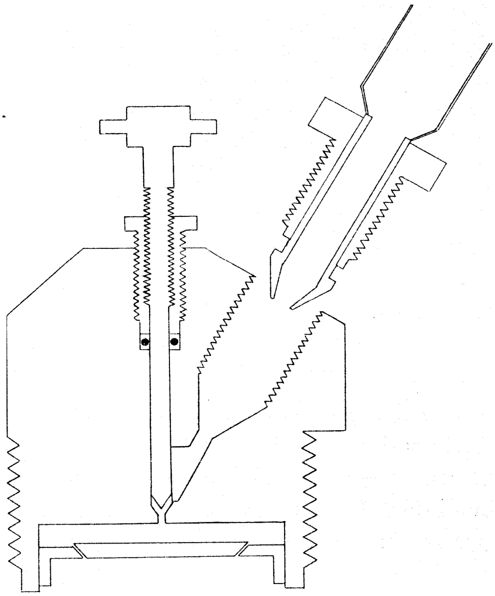
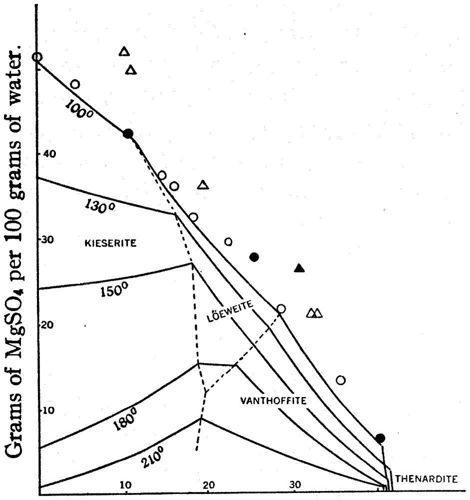


Fig. 3.—Cross section of upper part of bomb used for solubility determinations.

The behavior of a solution upon evaporation may be predicted from Fig. 4, which gives the isotherms at 100, 130, 150, 180 and 210°. The measurements of Archibald and Gale at 100° and of Mayeda at 103° are given on this diagram; our data are not given individually. Unless well seeded, the solution will be 10 to 20% supersaturated during concentration. Vanthoffite will not form under 95° unless a comparatively slow rate of concentration is employed. Appreciable amounts of kieserite will form if solutions supersaturated with respect to it are boiled for three hours or more, but with rapid evaporation its formation should be negligible. We sampled several freely boiling solutions which had deposited 10% by weight of salts and found them to be slightly more supersaturated than would correspond to the isotherm given by Archibald and Gale.



Grams of Na_2SO_4 per 100 grams of water.
○ Mayeda, 103°; △ Archibald and Gale. 100°;
A Univariant points.

Fig. 4.—Isotherms of the system.

The data are given in the table below. The first column gives the temperature and the second the reference, if the data are taken from previously published works. The third gives the experimentally determined fraction of magnesium sulfate of the total anhydrous salts in solution and the following column gives the average of the values. The fifth column gives the average value for the total salts, as grams per 100 g. of water, obtained by drawing a smooth curve through available data, as previously explained. The last two columns give the grams per 100 g. of water of magnesium and sodium sulfates.

TABLE II
COMPOSITIONS OF UNIVARIANT SOLUTIONS

Temp., °C.	Observer	$MgSO_4$ in total solids	Av.	Total solids, g./100 g H_2O	$MgSO_4$, g./100 g. H_2O	Na_2SO_4, g./100 g. H_2O
		Solid Phases: Epsomite and Mirabilite				
0		0.834	0.834	30.7	25.6	5.1
10	A. & G.	.737	.737	39.6	29.2	10.4
18.7	A. & G.	.635	.635	47.9	30.4	17.5
		Solid Phases: Epsomite and Astrakanite				
25	W. C. B.	0.620	0.620	51.8	32.1	19.7
30	Roozeboom	.660	.660	53.5	35.3	18.2
40	A. & G.	.767	.767	57.5	44.1	13.4
		Solid Phases: Mirabilite and Astrakanite				
25	W. C. B.	0.484	0.484	52.5	25.4	27.1
		Solid Phases: Mirabilite and Thenardite				
30	A. & G.	0,199	0.199	52.5	10.4	42.1

TABLE II (*Concluded*)

Temp., °C.	Observer	$MgSO_4$ in total solids	Av.	Total solids, g./100 g. H_2O	$MgSO_4$, g./100 g. H_2O	Na_2SO_4, g./100 g. H_2O
Solid Phases: Hexahydrate and Astrakanite						
50	A. & G.	0.847	0.847	58.6	49.6	9.0
55	D'Ans	.858	.858	58.5	50.2	8.3
60	A. & G.	.880	.880	59.5	52.4	7.1
Solid Phases: Thenardite and Astrakanite						
30	Roozeboom	0.346	0.346	55.2	19.1	36.1
50	A. & G.	.365	.365	57.2	20.9	36.3
65	D'Ans	.367	.367	57.2	21.0	36.2
75		.350 .351 .364	.356	56.2	20.0	36.2
86.5		.330 .329 .327	.329	54.7	18.0	36.7
90	D'Ans	.321	.321	55.2	17.7	37.5
Solid Phases: Astrakanite and Vanthoffite						
67		0.406	0.406	54.5	22.1	34.4
Solid Phases: Thenardite and Vanthoffite						
67		0.299	0.299	53.5	16.0	37.5
70		.284	.284	52.8	15.0	37.8
75		.250 .254	.252	51.0	12.8	38.4
76.5		.236 .236 240	.237	50.6	12.0	38.6
85		.188 .195	.191	48.5	9.3	39.2
86.5		.183	.183	48.2	8.8	39.4
95		.142 .151 .139 .141	.143	46.7	6.7	40.0
100		.127	.127	46.0	5.8	40.2
130		.052	.052	44.0	2.3	41.7
150		.0271	.0271	43.2	1.4	41.8
175		.0165	.0165	42.4	0.7	41.7
Solid Phases: Kieserite and Löweite						
70		0.869	0.869	58.0	50.4	7.6
75		.864	.864	56.9	49.2	7.7
85		.845 .858 .860 .862	.855	55.3	47.3	8.0
95		.812 .815	.813	53.6	43.6	10.0
100		.789 .798	.793	52.7	41.8	10.9
130		.676 .666	.670	49.6	33.2	16.4
148		.605	.605	46.0	27.9	18.1
180		.451	.451	33.7	15.2	18.5
Solid Phases: Loweite and Vanthoffite						
75		0.435 .440 .443	0.440	53.1	23.4	29.7
85		.442 .447 .449 .450	.447	51.5	23.0	28.5
95		.438 .437 .436	.437	49.7	21.7	28.0
100		.428 .438	.430	48.9	21.0	27.9
130		.407 .409	.408	46.7	19.0	27.7
150		.405	.405	42.7	17.3	25.4
180		.403	.403	38.9	15.7	23.2
Solid Phases: Kieserite and Vanthoffite						
		0.304	0.304	28.0		

The values in the third column are in each case those experimentally determined. Where the data of other observers have been employed, the most satisfactory value has been given in the table; the others have been given consideration in the construction of the initial diagram and the isotherms. The values given in this table are plotted in Fig. 1. They are not entirely concordant but sufficiently so to justify the construction of this type of figure. Owing to the limited number of measurements, the data above 100° cannot be considered as accurate as those at temperatures below the boiling point.

Summary

1. An apparatus has been developed with which equilibrium measurements in systems composed of two salts and water may be made at temperatures above the boiling point of the solution.

2. The literature relating to the system magnesium sulfate-sodium sulfate–water has been reviewed and presented along with new data obtained at temperatures between 67 and 210°.

3. The invariant point, löweite-hexahydrate-astrakanite-solution, has been found dilatometrically to lie close to 59.5°; and the invariant point, löweite-kieserite-vanthoffite-solution, to lie between 180 and 210°.

4. It has been shown that the disagreement in the previous data on this system between temperatures of 60 and 100° was probably caused by the extreme slowness with which the stable double salts come to equilibrium with their solutions.

5. The indentification of the salts occuring in this system by optical means has been discussed.

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[CONTRIBUTION PROM THE CHEMICAL LABORATORY OF RUTGERS UNIVERSITY]

THE VALUE OF THE HAGENBACH FACTOR IN THE DETERMINATION OF VISCOSITY BY THE EFFLUX METHOD

BY WILLIAM RIEMAN III

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Historical Introduction

For a more complete outline of the history of viscosity and in particular the value of the Hagenbach factor "m" in the kinetic energy correction, the reader is referred to Bingham's "Fluidity and Plasticity."[1] It is necessary to emphasize here only the following points. Numerous investigators have attacked the problem from the theoretical point of view, and have derived results identical in all respects except that the value of the constant m differs. None of the authors (prior to Bienias and Sauer-

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[1] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, 1922, pp. 1–21,

wald) have obtained experimental data to support their conclusions. Knibbs'[2] work in this field is unique. He devised an excellent mathematical treatment whereby m can be derived from experimental data, but instead of performing the necessary measurements himself he used Poiseuille's[3] data. The average value for m for 14 tubes is 1.135, with a mean deviation of ±0.153. Because of the large probable error this result cannot be regarded as an indisputable confirmation of Bousinesq's[4] theoretical value of 1.12.

For years the science of viscosimetry has been handicapped by lack of definite knowledge concerning this constant. Some scientists use Bousinesq's value, others prefer Couette's[5] value of 1.00. As Bingham suggests, the best method of avoiding serious error is to select a viscometer of such dimensions that the kinetic energy correction is only 1 or 2% of the entire viscosity. Then a small error in the constant will cause only an insignificant error in the final result. Recently N. E. Dorsey[6] has studied the configurations produced by a stream of colored liquid flowing from a circular capillary with smooth, square edges directly into the clear water contained in a reservoir. "All the distances from the terminus to the walls of the reservoir are severally so great that the distribution of the flow of the liquid is essentially the same as if they were infinite." His own observations and the data of W. N. Bond[7] led him to draw the following conclusions. The value of m is zero and the value of the Couette correction, λ, is 1.146 R when Reynolds' number[8] is less than 10. When Reynolds' number is greater than 10, two situations are possible; in one m is still zero and λ is 1.146 R; in the other m is a constant, probably 1, and λ is 0.573 R. When Reynolds' number exceeds 700, m decreases and approaches the value of 0.735. These values apply only to the ideal conditions; variations in the shape of the capillary or its ends or in the shape of the reservoirs may cause variation in the value of m and λ.

Dorsey also calculated the value of m from Poiseuille's data and found a value of 1.04. This is at wide variance with Knibbs' result. The author's calculations of Poiseuille's data agree with those of Knibbs.

The problem of the Hagenbach factor has been attacked recently from a new angle by Bienias and Sauerwald.[9] These authors are primarily

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[2] Knibbs, *J. Proc. Roy. Soc. N. S. Wales*, 29, 77 (1895).

[3] Poiseuille, *Mém. prés. par divers savants à l'acad. Roy. des Sci. de l'inst. de France*, 9, 433 (1846).

[4] Bousinesq, *Compt. rend.*, **113**, 49 (1891).

[5] Couette, *Ann. chim. phys.*, [6] 21, 433 (1860).

[6] Dorsey, *Phys. Rev.*, [2] 28, 833 (1926).

[7] Bond, *Proc. Phys. Soc. London*, 33, 225 (1921); 34, 139 (1922).

[8] $2\rho IR/\eta$, where I is the average velocity of the liquid in the capillary. See *Trans. Roy. Soc. London*, 174, 935 (1883).

[9] Bienias and Sauerwald, *Z. anorg. allgem. Chem.*, 161, 51 (1927).

interested in the viscosity of molten metals. Their viscometer was designed especially to meet the difficulties peculiar to this type of work and is not capable of as high a degree of accuracy as the instruments of Thorpe and Rodger,[10] or Bingham or other modern investigators. It consists essentially of a vertical capillary whose lower end is immersed in a bath of the metal contained in a carbon crucible. The upper end of the capillary is expanded into a bulb and is connected to a vacuum system and to a manometer. The determinations are made by applying suction and measuring the time required for the liquid to fill the bulb between two electrical contacts.

The dimensions of the apparatus are such that both the kinetic energy correction and the correction for varying hydrostatic head within the instrument must be applied. As Bingham[11] has demonstrated, when the hydrostatic pressure within the viscometer is greater than one-thirtieth of the pressure applied externally, it is not sufficiently accurate to consider the mean of the initial and final internal hydrostatic heads. We must consider the "chronological mean."[12] This value is greater than the mean of the initial and final values. In most viscometers the kinetic energy correction is necessary only at high velocities, whereas the correction for varying internal hydrostatic head is necessary only at low velocities. The necessity, encountered by Bienias and Sauerwald, of applying both corrections to the same measurement is unusual.

The procedure of Bienias and Sauenvald for the determination of m was as follows. Mercury at room temperature was sucked up into the viscometer and the time measured. Since the viscosity of mercury was known, all terms in the equation

$$\eta = \frac{\pi g P R^4 t}{8VL} - \frac{m\rho V}{8\pi L t}$$

were known or could be measured readily except m and P. The term P represents the pressure used to drive the liquid through the capillary. It is the difference between the manometer pressure, P„ and the chronological mean internal hydrostatic pressure, P_h,

$$P_m - P_h = \mathrm{P}$$

By assigning values to m we can calculate the value of P and hence of P_h. Dividing P_h by density, p, we get H, the chronological mean hydrostatic head.

The value of the chronological mean head was also determined by direct observation. The level of the mercury in the tube was measured at noted intervals of time. A curve between time and hydrostatic head was plotted and graphically integrated to obtain the chronological mean. This value ought to check the value calculated by the first method, pro-

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[10] Thorpe and Rodger, *Trans. Roy. Soc. London*, 185A, 397 (1894).

[11] Bingham, THIS JOURNAL, 38, 27 (1916).

[12] Bienias and Sauerwald call it "mittlere zeitliche Höhe."

vided the proper value of m was used in the calculation. The results of Bienias and Sauerwald are given in Cols. 1, 2, 3 and 4 of Table I.

TABLE I

RESULTS OF BIENIAS AND SAUERWALD

No.	Chron. mean head, cm. $m = 1$	$m = 1.12$	Chron. mean head by direct obs.	Probable error of calcd. value
1*	12.58	12.56	12.58	±0.02
2	12.29	12.24	12.29	± .04
3	12.18	12.10	12.17	± .05
4*	12.62	12.60	12.62	± .02
5*	12.30	12.24	12.28	± .04
6*	12.52	12.50	12.52	± .02
7	12.33	12.26	12.31	± .04
8	12.27	12.16	12.24	± .05
9*	12.81	12.78	12.80	± .02
10*	12.49	12.44	12.48	± .04
11	12.40	12.31	12.30	± .05
12	11.06	10.97	11.04	± .04
13	11.04	10.92	11.02	± .05
14	11.04	10.87	11.03	± .06

From these results Bienias and Sauerwald conclude that the correct value of m is unity.

A consideration of the errors involved in the work, however, reveals that their conclusion is not well established. They state that the probable error of their viscosity determinations is 1%. The same error would be attached to the determination of P by the method described above. Since P_h is obtained by subtracting P from P„ an error of 1% in P does not necessarily involve the same percentage error in P_h; but the probable error of P_h and H can readily be calculated. The results of these calculations are given in Col. 5, Table I. (The error in measuring the manometer pressure was assumed to be negligible.)

It is now obvious that the six results marked with an asterisk are meaningless, since the observed hydrostatic head (Col. 4) agrees with both calculated values (Cols. 2 and 3) within the limit of error of the latter values. In the majority of the remaining cases the probable error is so large, compared with the other differences, that very little dependence can be placed on the results. In one case (No. 11) the value, $m = 1.12$, gives the better agreement.

From these considerations it is evident that the conclusions of Bienias and Sauerwald concerning the value of m are drawn from meager, inaccurate and, in part, contradictory data. Apparatus designed for use with molten metals is not suitable for an accurate determination of the Hagenbach factor.

Apparatus

The work described herein had as its sole objective an accurate and reliable determination of m under experimental conditions similar to those generally used by modern investigators in the determination of viscosity.

The apparatus, in general design, is so similar to that recommended by Bingham,[13] that a detailed description is not necessary.

The viscometer, however, is somewhat different. Since it is desirable to change the capillary it was not fused into the viscometer but attached in a horizontal position to the two limbs of the instrument with stout rubber tubing. Since no change in working volume of liquid could be detected during use, we can feel certain that no appreciable leak occurred at the joints. In all other respects, such as traps, shape of bulbs, etc., the viscometer resembled Bingham's. It was immersed in a well-stirred water-bath whose temperature was automatically controlled within a few hundredths of a degree.

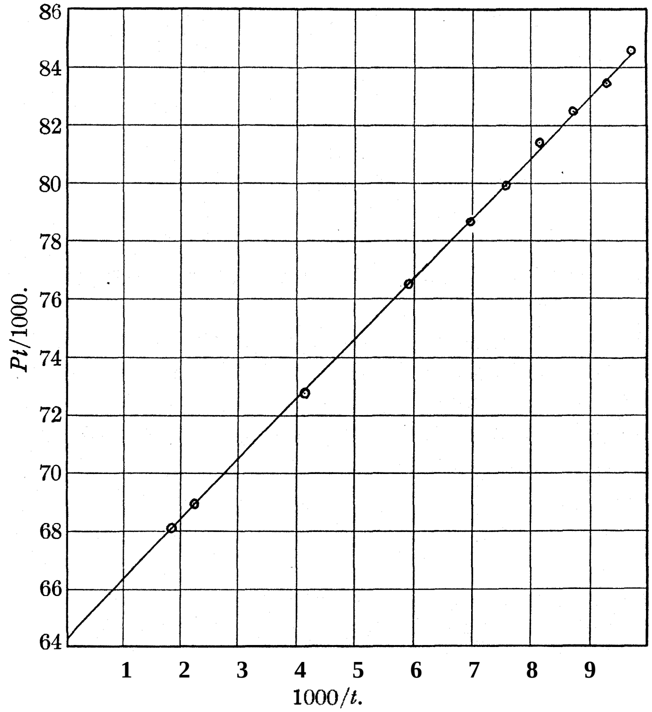

Fig. 1.

The volume of the viscometer and the dimensions of the capillary were selected so that at high pressures the kinetic energy correction, $m\rho V/8\pi Lt$ would be a large fraction, $^1/_7$ to $^1/_4$, of the uncorrected viscosity, $\pi gPR^4t/8VL$. At the same time care was taken to avoid the critical velocity and to avoid the use of apparatus too small to allow accurate measurements.

[13] Ref. 1, pp. 67 and 295–311.

Procedure

The volume of the bulb of the viscometer was carefully measured The capillary was selected and the edges were ground perpendicular to the axis. The length was measured with a micrometer caliper. The capillary was then attached between the limbs of the viscometer with heavy rubber tubing. The viscometer was filled with water and the time of efflux measured under a pressure of about 850 g. per sq. cm. This determination was run in duplicate or triplicate. Then the pressure was reduced somewhat, all other conditions remaining the same, and the time again measured. This process was repeated until a series of about ten readings was obtained for which only the pressure and time varied.

These results were then treated mathematically by the method of Knibbs. The equation is put in the form

$$Pt = \frac{8\eta VL}{\pi g R^4} + \frac{m\rho V^2}{\pi^2 g R^4}\cdot\frac{1}{t}$$

The values of Pt are plotted as ordinates and the values of $1/t$ as abscissas. From the above equation it is evident that if m is constant, the curve should be a straight line. Within the very small experimental error it was found to be such.

The intercept on the Y axis represents the value of Pt when the time is infinite, that is, when the kinetic energy is zero. Then

$$Pt = \frac{8\eta VL}{\pi g R^4}$$

Since the viscosity of water is known, we can use this equation to calculate the value of R. This gives a value of much greater precision than can be attained by microscopic measurement or by weighing a mercury slug.

The slope of the line, s, is equal to the coefficient of $1/t$.

$$S = \frac{m\rho V^2}{\pi^2 g R^4}$$

By use of this equation the value of m can be calculated.

Results

As an example of the method of plotting and calculating the value of m, the complete data for Series 6 are given in Table II.

TABLE II

COMPLETE DATA FOR SERIES 6

Detn. no.	P	t	$Pt/1000$	$1000/t$	Reynolds' number
1	826.3	102.35	84.57	9.770	1013
2	773.7	107.9	83.48	9.268	961
3	718.8	114.8	82.51	8.711	903
4"	662.2[a]	123.0[a]	81.45[a]	8.130[a]	843[a]
5	605.8	131.9	79.91	7.582	786
6	548.6	143.4	78.67	6.974	723
7	452.0	169.3	76.52	5.907	613
8	301.0	241.8	72.78	4.136	429
9	160.0	431.0	68.97	2.320	240
10	126.2	539.8	68.11	1.852	192

Temp. = 36° η = 0.007085 V = 10.018

L = 1.9278 g = 980.2 p = 0.9937

[a] Reject these values. High value for time, probably because of dust caught in capillary.

The results are plotted in Fig. 1.[14] From the figure we can see that the Y intercept is 64.173.

$$64{,}173 = \frac{8 \times 0.007085 \times 10.018 \times 1.9278}{\pi \times 980.2\, R^4}$$

Solving for R we find that $R^4 = 0.55394 \times 10^{-8}$ or

$$R = 0.0086270 \text{ cm.}$$

From the figure the slope is 2.089.

$$2{,}089{,}000 = \frac{m\ 0.9937\ (10.018)^2}{\pi^2\ 980.2 \times 0.55394 \times 10^{-8}}$$

$$m = 1.122$$

A summary of all the results obtained up to the present time is given in Table III.

TABLE III

SUMMARY OF RESULTS

Series no.	Cap.	L	Temp., °C.	$R\mu$	m
1	1	0.8096	25.00	52.463	1.110
2	1	.8096	22.00	52.498	1.127
3	1	.8096	36.10	52.467	1.134
4	1	.8096	25.00	See below	1.128
5	2	1.9278	34.00	86.278	1.124
6	2	1.9278	36.00	86.270	1.122

V = 10.018; av. m = 1 124; av. deviation = ±0.006.

In Series 4, methanol was used instead of water. A c. P. sample was further purified by fractional distillation and the portion distilling between 64.46 and 64.51' was collected for use. Its density was 0.79158 at 20° and 0.78695 at 25° Because of uncertainty concerning the viscosity of methanol and also because of the possibility of impurities in the sample used, no attempt was made to calculate R in this determination. Instead, the average of the three previous values was used for the calculation of viscosity. The viscosity was found to be 0.005508 at 25°. Interpolating the results of Thorpe and Rodger to the same temperature, we find a value of 0.005527. Since Thorpe and Rodger took more care in the purification of their sample, their result is probably more nearly correct. It should be noted, however, that Thorpe and Rodger used 1 for the Hagenbach factor. If they had used the value, 1.12, their result would have been 0.005521.

Microscopic Measurements.—Although microscopic measurements of the capillary radius are not sufficiently precise for use in the calculation of m, they must be used to gain knowledge concerning the shape of the capillary. The two ends of the thermometer tubing, which before break-

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[14] In drawing the line which runs through the points with the minimum error, the graphical method cannot be considered sufficiently accurate. The mathematical treatment given on p. 327 of Mellor's "Higher Mathematics for Students of Chemistry and Physics," 4th edition. Longmans, Green and Co., New York, 1913, was used.

ing were in juxtaposition to the portion used in the viscometer, were used to prepare cross-section slides for the microscope. From these slides the major and minor axes of both ends of the capillary were determined by use of a filar micrometer. It was assumed that the cross section was elliptical, a fact which was supported by the appearance of the slide under the microscope. The formula of Knibbs

$$R = \sqrt[4]{\frac{3R_1^3R_2^3}{R_1^2 + R_1R_2 + R_2^2} \cdot \frac{(1 - e^2)^3}{1 + e^2}}$$

was used to calculate the value of R which should be used in the viscosity equation. In this formula, R_1 is the arithmetical mean of the semi-axes at one end, R_2 is the mean of the semi-axes at the other end; e is $(B - C)/(B + C)$, where B is the mean of the major axis and C is the mean of the minor axis. The results are given in Table IV.

TABLE IV

RESULTS

	Capillary 1	Capillary 2
End A. Major radius, μ	53.78	95.20
End A. Minor radius, μ	50.82	79.45
End B. Major radius, μ	54.20	95.20
End B. Minor radius, μ	50.46	79.35
R by micrometry	52 26	86.60
R by viscometry	52.476	86.274

The slight differences in the values of R obtained by the two different methods are due to errors in the microscopic measurements or to irregularities in the capillary between the two ends.

Discussion of Results

Precision.—In the individual measurements of length, volume, time and pressure, the precision varied from about 0.01 to 0.1%. Since the maximum internal hydrostatic pressure was less than one-thirtieth of the manometer pressure, the correction for varying internal head is less than the experimental error and can be omitted. The value of R^4 as determined by the viscosimetric method is attended by an error probably not greater than 0.1%. The percentage probable error of m is greater than that of R^4 in about the ratio, kinetic energy correction at high pressures to uncorrected viscosity. That is, the percentage probable error of m is 4 to 7 times that of R^4 or about 0.4 to 0.7%. This agrees with the mean deviation of m.

To the length, as actually measured, some investigators add the Couette end correction, nR, where n is a constant. Couette originally assigned to n a value of 6. More recent investigation indicates that the correction is much smaller, perhaps even zero. The correction has not been applied in our calculations because of the uncertainty of the correct value of n

and because it has only an insignificant effect on the calculated value of m. For example, if we use Dorsey's value ($n = 0.573$) in calculating the data of Table II we find $m = 1.125$, or 0.003 greater than the value calculated without the Couette correction.

Conclusions.—Within the range studied the value of m is 1.124 ± 0.006. This agrees with the theoretical value of Bousinesq, 1.12, within the experimental error. The question arises whether this result may be applied to other tubes and other liquids.

The choice of liquids was restricted to those which do not attack rubber. Although only two were used in this investigation, there is no reason to believe that the value of m depends on the nature of the liquid.

The shape of the capillary may affect the value of m. In this investigation an effort was made to secure capillaries which were as nearly as practical right circular cylinders. Therefore, we are not entirely justified in extending the value, $m = 1.12$, to capillaries which deviate from the ideal shape more than the capillaries described here. Let us consider two possible manners of deviation from the right circular cylinder.

In the first place the capillary may be a frustum of a cone, that is, the cross-sectional area may be different in different parts of the tube. In a capillary of uniform cross section the loss of kinetic energy occurs only at the ends. In a conical tube, however, there would also be a loss or gain of kinetic energy inside of the capillary. Consequently, it is possible that the Hagenbach factor may have a different value in conical tubes. The capillaries used in this investigation had almost uniform cross sections.

In the second place, the cross section, although uniform throughout the length of the capillary, may be elliptical rather than circular. Indeed, it is impossible to find thermometer tubing of perfectly circular bore. The capillary cross section of greatest deviation from the circle was end B of capillary 2, with an eccentricity of 0.553.

The shape of the ends of the capillary and the shape and size of the reservoir may also affect the value of m. The exit reservoir of our viscometer differed widely from the ideal conditions described by Dorsey. The liquid leaving our capillary flowed into a trap, provided for the settling of dust particles, then into a bulb, provided to facilitate the adjustment of the working volume, and finally into the larger bulb of measured volume. This difference in reservoirs may account for the difference between our results and Dorsey's.

It should be noted, however, that our viscometer is fundamentally similar to the viscometers used by Thorpe and Rodger and other investigators who are interested in the practical determination of viscosity rather than the theoretical laws of flow under ideal conditions. Therefore, it is very probable that the value, $m = 1.12$, is the correct one to be applied to instruments like those of Thorpe and Rodger and Bingham. Our data do not support Dorsey's view that m decreases when Reynolds' number exceeds 700.

Further investigations are being conducted in this Laboratory to determine the value of m for capillaries of other shapes.

Summary

1. Within the range of experimental conditions studied, the Hagenbach factor has been found to be **1.124** ± 0.006.
2. The viscosity of methanol at 25° has been determined and a value obtained which agrees with the value of Thorpe and Rodger within 0.3%.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY AND THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

CHEMICAL AFFINITY IN METALLIC ALLOYS, ESPECIALLY SOLID SOLUTIONS: A STUDY IN COMPRESSIBILITY

BY ROBERT FRANKLIN MEHL[1] AND BEVERIDGE JAMES MAIR[2]

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The study of the properties of solid solutions is one of the chief aims of metallurgical science. Its practical importance is evidenced by the fact that of the alloys useful because of their superior mechanical properties most are wholly or partly solid solutions. Numerous researches[3] have shown that, with one or two exceptions,[4] terminal solid solutions are simple in structure, showing the space lattice of the solvent metal only, the atoms of the solute having simply replaced atoms of the solvent; intermediate solid solutions are more complicated in structure. The behavior, physical and chemical, of the lattice so modified is, therefore, dependent upon the interaction of the different atoms, and this will be intimately related to their different chemical natures, and also to their specific crystallographic tendencies. From a chemical standpoint the chief effect of interest is that of a partial fixing of the valence electrons, an effect to be expected from the normal chemical affinities between the unlike atoms, and indicated by the enormous decrease in electrical conductivity resulting from solid solution formation. From a mechanical point of view the interaction between unlike atoms is presumably intimately related to the large increase in hardness observed.

Such a partial fixing of the valence electrons is of course not stoichio-

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[1] National Research Fellow.

[2] Contributor to the experimental work on compressibility only.

[3] See G. L. Clarke, "Applied X-Rays," McGraw-Hill Book Co., New York, 1926, page 204.

[4] Notably iron-carbon, manganese-carbon and perhaps copper-tin (see page 66).

metric, and the chemical affinities operative in solid solutions are more nearly like those governing adsorption than like those in saline compounds. The factors determining the composition of intermetallic compounds (which exhibit apparently ambiguous valence relations) have not been explained, though for a complete valence theory such an explanation is obviously necessary. These compounds are highly crystalline, and their heats of formation indicate that the chemical forces at play are commensurable with those in saline compounds.[5] In fact, evidence has been presented[6] in proof of the salt-like nature of certain of these compounds.

Whatever the nature of the chemical forces governing the composition of the intermetallic compounds, it seems reasonable that similar forces should be operative in metallic solid solutions, and it appears likely that an evaluation of the magnitude of these forces should be of value in explaining the behavior of solid solutions, especially the electrical and mechanical, and that ultimately a study of these forces should be of value to the study of chemical affinity in general and the solid state in particular.

It may be said (somewhat truistically) that two metals form solid solutions when the potential energy of their atoms in the state of solid solution is less than that in the elementary states. The problem of measuring the tendency of two metals to form solid solutions (the answer to which would explain quantitatively the phenomenon of limited miscibility) is therefore the problem of evaluating this potential energy decrease. Such an analysis does not now seem possible, though the recent work on lattice energetics may finally lead to this. To be orthodox chemically, such a measurement should be in terms of free energy decrease. For a solid alloy the only practicable method is that involving a measurement of the heat of formation of the alloy and the specific heats of the component metals and of the alloy over a wide temperature range.[7]

[5] Biltz, *Z.* anorg. Chem., **134,** 37 (1924); 140, 261 (1924).

[6] Owen and Preston, *Proc. Phys. Soc. London, 36,* 14 (1923).

[7] Considerable time was spent in attempting to evaluate this quantity calorimetrically. The simplest and most general method for determining the heat of formation is to dissolve the alloyed and the unalloyed metals in similar quantities of a solvent in a system of known heat capacity, and by the difference in the temperature rises observed in the two cases to calculate the heat of formation by application of the law of constant heat summation. The method has been applied especially to intermetallic compounds6 and to the copper–zinc system, exclusive of the a-solid solutions [Baker, *Z. physik.* Chem., **38,** 630 (1901)]. The adiabatic calorimetric method developed by Richards [THIS JOURNAL, 32, 431 (1910)] was used, with hydrochloric acid as a solvent.

The most advisable course seemed to be to investigate those terminal solid solutions in which cubic metals play the role of solvent. Accordingly a series of the a-aluminum-magnesium alloys was prepared. The calorimetric system, including 941.4 g. of $HCl\cdot 20H_2O$, had a heat capacity of 810.0 cal./deg. The reaction between the elementary magnesium and the acid (in the blank determination) was slowed by partly lacquering the magnesium particles (which were roughly $^1/_8''$ in diameter) and by imprisoning them

The e.m.f. method is apparently inapplicable because of the practical difficulty in setting up a cell representing the reaction between the component metals to give an alloy of the composition desired, though the Nernst-Reinders theory[S] of the equilibria between solid solutions and aqueous solutions of salts of the component metals appears to make such a determination possible, when the solution pressures of the component metals are not too greatly different.[9] However, because of the difficulties in obtaining a reversible electrode truly representative of the composition of solid solution desired, it is unlikely that the e.m.f. method will be of value for this purpose.

in an inverted platinum cone wired to the bottom of the platinum wire basket. **A** drop of chlorplatinic acid served to catalyze the dissolution of the aluminum.

Before making any determinations on alloys, the heat of solution of magnesium in $HCl \cdot 20.05H_2O$ was determined. Three determinations using **0.7481** g. of magnesium in each gave temperature rises of **4.193, 4.189** and **4.192°,** an average of **4.191°** which, multiplied by **810.0 cal./deg.,** gives **2594.7** cal. at a temperature of **20".**

The aluminum-magnesium alloys were prepared in an apparatus similar to one previously developed by one of the authors [Mehl, ***Trans. Amer. Electrochem. Soc.,*** **46,** October, **1924)** except that argon instead of hydrogen was used for an atmosphere. After preparation the alloys were annealed for **24** hours just below their melting points. The synthetic compositions of the alloys prepared were **5.5, 8.0** and **9.0** percentage of magnesium by weight. The temperature rises observed for **0.6948** g. of each composition were, respectively, **3.964, 3.957** and **3.961".** The blank determinations, using equivalent quantities of the unalloyed metals, gave, for the same compositions, **3.961, 3.963"** and **3.960°,** apparently identical with the first.

The sensitivity of the calorimetric method as applied to these alloys is probably around **0.006°,** indicating that the heat of formation of the a-solid solution in this system is probably less than **8** cal. per gram.

A similar series of measurements was carried out on the or-solid solutions in the aluminum–zinc system, though the method is less satisfactory in its application to these alloys, for it takes approximately **7** g. of zinc to give the desired four degrees rise, as contrasted to **0.7** g. of aluminum. Any segregation in the alloy, therefore, leads to **greatly** different heats of solution when constant weights of the alloys are dissolved. Prolonged annealing of the castings prevented such segregation in considerable degree, but it soon became apparent that another disturbing factor was present. An alloy of **14.49%** of zinc by weight, quenched after twenty-four hours' annealing at **575°,** gave a temperature rise of **4.057° (0.8050** g.); after a month this had fallen to **3.988°.** An alloy of **19.27%** of zinc by weight, quenched after twenty-four hours' annealing at **550°,** gave **4.053" (0.8500** g.); after a month this had fallen to **3.990'.** It therefore appears that there is some transition in this region of the system, possibly the precipitation of the β-solid solution, resulting in a lower heat content. This point, however, was not the immediate, and the work was abandoned as unfruitful. It is to be noted that the interesting magnesium–cadmium system could be investigated by this method, but only **if** sufficient refinement of method were developed, for the investigation of this system is likewise made difficult by the disparity in the heats of solution of the component metals.

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[8] Nernst, *Z. physik. Chem.,* **22, 539 (1897);** Reinders, **ibid., 42,225 (1902).**

[9] In the case of the a-solid solution in the copper–zinc system, for example, the aqueous solutions of the mixed sulfates of copper and zinc in equilibrium with the solid solution would contain only a trace of the copper ion.

Any measurement of chemical affinity which does not determine free energy change must be considered indirect and from the standpoint of chemical theory less valuable. Such a criticism may be made of the following study, in which changes in compressibility are investigated, but it will be seen that the compressibility point of view has some distinct and unique advantages as applied to metal systems.

The Compressibility of Metallic Alloys, Especially Solid Solutions

That compressibility is a property directly related to the cohesive forces in solids has been repeatedly emphasized by Richards.[10] In elementary solids these cohesive forces are physical in the sense that electrochemical effects involving the displacement of electrons are absent. In compounds the increase in cohesion caused by chemical interplay between unlike atoms is manifested by a decrease in compressibility. This basic idea is very simple in its application to alloys, especially to terminal solid solutions of the simple substitutional type, for here the components in almost every case are solid at room temperature and the effect of the chemical affinity between the unlike atoms may be shown simply by the difference between the compressibility of the unalloyed metals and that of the alloy. That such a comparison leads to results which are of some value to present metallurgical science may be seen in the following.

Some measure of success was assured this work by two determinations made by Adams, Williamson and Johnston,[11] in the course of their investigations of the compressibility of various solids, upon an α-brass and a tin-bismuth alloy. The first was found to give a compressibility coefficient much lower (25%) than the rule of mixtures value, and the second a coefficient very close (within 5%) to the calculated value. No explanation of these results was attempted, except to point out that the copper–zinc system exhibits physical properties which "do not bear a simple relation to the properties of the end members of the series," whereas in the tin–bismuth system many of the physical properties vary linearly with the composition.

The earlier results of Regnault[12] and of Amagat[13] on steel and brass are not comparable in accuracy with modern data.

The extensive work of Lussana on metal systems[14] shows little connection between compressibilty and constitution and in certain cases indicates compressibility coefficients for terminal solid solutions greater than the

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[10] (a) Richards, *Proc. Amer. Acad. Arts Sci.*, 39, 603 (1904); (b) THIS JOURNAL, 36, 2417 (1914); (c) *J. Franklin Inst.*, 198, 25 (1924); (d) *Chew. Rev.*, 2, 315 (1925).

[11] Adams, Williamson and Johnston, THIS JOURNAL, 41, 12 (1919).

[12] Regnault, *Mem. de l'acad. des sciences, 26,* 229 (1847).

[13] Amagat, *Compt. rend.*, 108,1199 (1899); *J. phys.*, [2] 8, 197,358 (1899).

[14] Lussana, *Nuovo Cimento,* [5] 19, 187 (1910). See also "Piezochemie Kondensierter Systeme," by Cohen and Schut, Leipzig, 1919, page 139.

rule of mixtures values.[15] An inspection of his data for the pure metals discloses the fact that they disagree with the best modern data from —37% for aluminum to +64% for lead, and also indicate abnormal temperature coefficients.[16] It seems necessary to conclude from this that Lussana's data are not to be compared in accuracy with the best of modern data, though there is a qualitative agreement. But for the investigation of alloys, where the difference between the calculated (rule of mixtures) value and the observed value is the datum sought, a difference including three experimental inaccuracies, one for each of the component metals and one for the alloy, measurements of high accuracy are essential.

Bridgman[17] has given a value for the compressibility of commercial nichrome wire and also a value for steel, which will be considered later. E. Madelung and R. Fuchs[18] have published values for brass and for steel.

Beckman[19] determined the compressibility for a series of silver-gold alloys. The coefficient given for pure gold, 1.55×10^{-6}, however, is greatly in excess of Bridgman's, 0.572×10^{-6}, and the value extrapolated for pure silver is 1.50×10^{-6}, also greatly in excess of Bridgman's value, 0.987×10^{-6}.[20]

So far as the authors are aware these are the only published data on the direct determination of the compressibility of alloys. Compressibility coefficients have been calculated for a number of alloys from the modulus of elasticity in tension (E, Young's modulus) and the modulus of elasticity in shear (C, the modulus of transverse elasticity or rigidity),[21] especially by E. Grüneisen.[22] Although the compressibility coefficients obtained in this way agree well with those determined directly, except for the soft metals, the method is of less general applicability because of its sensitivity to plastic flow, to slight inhomogeneities in the structure of the material

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[15] For example, Lussana's value for an alloy of copper-aluminum, 7% by weight (20% by volume) aluminum, an α-solid solution, is 1.19×10^{-6} between 1 and 1000 atm. whereas the calculated value is 0.88×10^{-6}. In this system seven values are in excess of the rule of mixtures values and only one below.

[16] Lussana gives 0.88×10^{-6} for the compressibility of aluminum at 2000 atm. and 14.7°, whereas Richards gives 1.47×10^{-6} (corrected in the present work to 1.40×10^{-6}) over a range of 100 to 500 megabars at 20°, and Bridgman gives 1.334×10^{-6} at 30° and zero pressure. Lussana gives 0.96×10^{-6} for the same metal at the same pressure and at 27.0' whereas Bridgman finds 1.391×10^{-6} at 75°, an increase of only 4% over a temperature range of 45'. Lussana's value for lead at 500 atm. and 10° is 3.81×10^{-6} whereas Richards finds 2.33×10^{-6} at 20° between 100 and 500 megabars.

[17] Bridgman, *Proc. Amer. Acad. Arts Sci.*, **58**, 5 (1923).

[18] Madelung and Fuchs, *Ann. Physik*, [4] 65,289 (1921).

[19] Beckman, *Dissertation*, Upsala, 1910; International Critical Tables, Vol. II, 215.

[20] The original of this paper was not available. The method of measurement used by Beckman is unknown to the authors.

[21] Compressibility $= \beta = 9C - 3E/CE = 3(1 - 2\sigma)/E$, where σ is Poisson's ratio.

[22] Grüneisen, *Ann. Physik*, 22,801 (1907); 25,825 (1908).

measured and because of the apparently great difficulty in applying it to the very brittle intermetallic compounds. In addition it gives no indication of the variation of the compressibility with pressure. Grüneisen determined the compressibility of iron, steel, constantan and manganin. G. Angenheister[23] carried out similar measurements on alloys of silver and copper, but the values calculated from his data for the compressibilities of silver and copper, 0.80×10^{-6} and 0.58×10^{-6}, do not agree with those of Grüneisen (0.92×10^{-6} and 0.74×10^{-6}, respectively). The compressibilities calculated for the intermediate compositions show a decided departure from the rule of mixtures values. A minimum comes at 50% by volume and indicates a maximum decrease from the calculated value of 0.26×10^{-6} (from 0.70×10^{-6} to 0.44×10^{-6}). The curve obtained is gently sagging throughout its course and shows no critical points at the limits of solid solubility (copper dissolves 1% by volume of silver and silver 7% copper). The curve shows a progressive departure from a straight line in the heterogeneous fields, where linearity should be strictly observed.

It is clear, therefore, that there are not sufficient data available for the study of the cohesive forces in alloys by means of compressibility. In order to satisfy this lack the present work was undertaken, but as a preliminary study only, for a complete set of data for binary alloys would require investigation of over 400 binary systems. In order first to survey the field, a number of typical alloys was chosen, with the hope that the results would be sufficiently illuminating to indicate the most fertile paths for additional research.

Experimental

Method of Measurement.—The method and apparatus developed by Richards[24] were used without modification. Measurements were made at 25° and required the use of a correction factor for water previously determined by the authors.[25] The piezometers used were of the usual type, sufficiently large to hold an alloy piece with a volume of 25 $cm.^3$. Duplicate determinations were made on each alloy except certain intermediate solid solutions and intermetallic compounds. Divergent results almost always could be traced to the accidental introduction of impurities into the piezometer capillary and when such was the case the results were discarded. Divergencies which could not be traced to such experimental imperfections were discredited by a sufficient number of consistent determinations. In each case, however, the divergent results are noted in the table of data.

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[23] Angenheister, Ann. *Physik,* [4] 11, 188 (1903).

[24] (a) Richards, ref. 10a; (b) THIS JOURNAL, 46, 935 (1924). Experimental details are given in full in these papers.

[25] Mehl and Mair, *ibid.*, 49, 1892 (1927).

Materials.—The preparation, heat-treatment and analysis of the alloys presented a task impossible of accomplishment within the time at our disposal, and it was only through the kindly help of a number of industrial metallurgists that the work was made possible; several of the alloys were given additional treatment after their receipt. Table I lists the alloys investigated, with the percentage composition by weight and by volume, and with the heat and mechanical treatment noted for each alloy.

Each alloy was machined into a cylindrical bar 1.516 cm. in diameter and 13.8 cm. long, except the brittle intermetallic compounds, which were cast in graphite tubes.

TABLE I

ALLOYS INVESTIGATED

Alloy	Composition		
no.	by weight	by volume	Treatment
1	55% Cu; 44% Ni; 1% Fe	55% Cu; 44% Ni; 1% Fe	Cast; rolled; annealed at 1000° for 3 hours
2	36.27% Ni; 63.24% Fe; 0.15% C; 0.49% Mn; 0.15% Si; 0.05% Cr	33.7% Ni; 65.6% Fe; 0.7% Mn	Forged
3	92.34% Cu; 7.66% Al	78.4% Cu; 21.6% Al	Slightly hot-rolled; drawn cold to 0.705' from 1.000"; annealed 1 hour at 850°
4	87.1% Cu; 12.9% Al	66 9% Cu; 33.1% Al	Hot-rolled to 0.705' from 1.000'; annealed 1 hour at 850° and quenched in water
5	81.94% Cu; 17.95% Zn; 0.06% Pb; 0.05% Fe	78.5% Cu; 21.5% Zn	Cast; annealed 1 hour at 810°; cold-rolled to $12^1/_2\%$ reduction in height (to $^3/_4$" bar); annealed 2 hours at 500°
6	64.27% Cu; 35.61% Zn; 0.09% Pb; 0.03% Fe	59.0% Cu; 41.0% Zn	Cast; annealed 3 hours at 700°; cold-rolled to $12^1/_2\%$ reduction in height: annealed 2 hours at 500°; cold-rolled to $16^1/_2\%$ reduction in height (to $^3/_4$" bar); annealed 2 hours at 600°
7	51.43% Cu; 48.57% Zn; 0.06% Pb; 0.04% Fe	45.8% Cu; 54.2% Zn	Cast; hot-rolled at 600°; annealed 2 hours at 500°; heated to 800.°, cooled to 600° and quenched in oil
8	88.53% Cu; 11.44% Sn; 0.03% Fe	86.3% Cu; 13.7% Sn	Cast; annealed 10 hours at 600°; cold-rolled to 20% reduction in height; annealed 2 hours at 650°
9	61.16% Cu; 38.78% Sn; 0.06% Fe	56.3% Cu; 43.7% Sn	Cast in hot graphite tube; annealed 3 hours at 500°
10	67.43% Cu: 32.53% Sn; 0.04% Fe	62.8% Cu; 37.2% Sn	Cast in hot graphite tube; annealed 3 hours at 500°
11	87.24% Al; 12.56% Mg; 0.085% Si; 0.12% Fe	81.7% Al; 18.3% Mg	Extruded; annealed at 430° for 18 hours

TABLE I (*Concluded*)

Alloy no.	Composition by weight	Composition by volume	Treatment
12	99.941% Al; 0.013% Si; 0.022% Fe; 0.022% Cu; 0.002% Ti		Cast
13	96% Cu; 4% Si	86.6% Cu; 13.4% Si	Cast; annealed 4 hours at 850°; hammered on anvil to reduce diameter of bar from 0.723' to 0.690'
14	0.89% C; balance Fe (Armco iron base)		Cast; heated to 900°; quenched in cold water
15	Same as 14		Heated to 940° and cooled at a uniform rate to 480° over a period of $3^1/_2$ hours
16	1.36% C; balance Fe (Armco iron base)		Cast; heated to 900°; quenched in cold water
17	Same as 16		Heated to 940° and cooled at a uniform rate to 480° over a period of $3^1/_2$ hours

Experimental Results.—Two piezometers were used, numbered 1 and 2. Table II gives the standardization data for each. The validity of the standardizations is attested by the agreement among the various separate determinations and also by the agreement between the compressibilities measured and the results obtained by other investigators. All measurements were made at 25°. Two values are given for the quantities of mercury corresponding to a pressure range of 100 to 500 megabars: one was obtained in passing from 500 to 100 megabars, and the other in

TABLE II

PIEZOMETER STANDARDIZATION DATA

Piezometer No. 1			Piezometer No. 2		
Wt. of water	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars calcd. to common quantity of water: 2.7928 g.	Wt. of water	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars calcd. to common quantity of water: 3.1993 g.
2.7928	0.7973	0.7973	3.1993	0.8971	0.8971
	.7966	.7966		.8971	.8971
2.6873	.7764	.7981			
	.7768	.7985	3.2347	.9031	.8959
				.8997	.8925
2.5051	.7350	.7938	2.4985	.7486	.8918
	.7420	.8008		.7490	.8922
2.7236	.7862	.8003			
	.7790	.7931		Average	.8945
0.8928	.4058	.7942			
	.4024	.7908			
	Average	.7964			

passing from 100 to 500 megabars. The agreement within these pairs is a criterion of the success of the individual determinations. The separate standardizations were converted to a common quantity of water by the use of the water correction factor previously determined by the authors.[25]

TABLE III

No. of alloy	No. of piezometer	Wt. of water	Wt. of alloy	Density of alloy	Wt. of mercury, 100–500 megabars	Wt. of mercury, 100–500 megabars corr. to piezometer water standard	$\beta \times 10^6$
1	2	2.8120	222.406	8.910	0.3777 .3813	0.4569) .4605	0.60 .62
1	2	2.8200	222.406	8.910	.3777 .3791	.4566 .4552	.64 .63
1	2	2.6580	222.406	8.910	.3464 .3466	.4572 .4670	.62 .63
2	2	3.0715	199.867	8.402	.4608 .4618	.4868 .4878	.85 .84
2	2	3.2611	199.867	8.402	.5018 .5022	.4891 .4895	.85 .85
3	1	2.4564	194.49	7.847	.2811 .2793	.3499 .3481	.68 .67
3	2	3.1550	194.49	7.847	4 5 4 .4545	.4636 .4636	.79 .80
3	2	2.7773	194.49	7.847	.3717 .3745	.4580 .4608	.75 .77
4	1	2.4631	178.76	7.244	.3008 .2974	.3682 .3648	.80 .78
5	1	2.2340	214.53	8.669	3 .2457	3 5 7 4 .3599	.73 .75
5	1	2.0723	214.53	8.669	.2110 .2171	.3583 .3644	.74 .78
6	1	2.3273	209.03	8.426	.2724 .2685	.3675 .3636	.81 .78
6	1	2.3000	309.03	8.426	.2791 .2681	.3798 .3688	.91 .82
7	1	2.4564	202.95	8.291	.4515	.4083	.93
8	1	2.6398	212.90	8.631	.3421	.3734	.84
8	1	2.5061	212.90	8.631	.3168 .3144	.3754 .3730	.85 .84
9	1	4.7582	201.38	9.024	.8338 .8304	.4321 .4287	.99 .96
10	2	4.9141	206.24	8.931	.8528 .8556	.5023 .5051	.88 .90
11	1	2.6887	63.16	2.553	.4490 .4454	.4703 .4667	1.57 1.55
11	1	2.5151	63.16	2.553	.4070	.4638	1.52

TABLE III *(Concluded)*

No. of alloy	No. of piezometer	Wt. of water	Wt. of alloy	Density of alloy	Wt. of mercury, 100–500 megabars	Wt. of mercury. 100–500 megabars corr. to piezometer water standard	β X 10⁶
12	2	3.3096	66.67	2.702	.5670	.5445	1.39
					.5644	.5419	1.37
12	2	3.3053	66.67	2.702	.5672	.5455	1.39
					.5714	.5497	1.43
12	1	2.4649	66.67	2.702	3 8 0	.4477	1.40
					.3798	.4468	1.39
13	1	2.6564	207.44	8.406	.3646	.3925	.98
					.3620	.3899	.96
13	1	2.6564	207.44	8.406	.3582	.3861	.94
14	2	3.5408	189.61	7.798	.5184	.4486	.62
14	2	3.4924	189.61	7.798	.5104	.4505	
					.5064	.4465	.62
15	1	4.2588	181.50	7.835	.6871	.4705	.60
15	1	4.3995	181.50	7.835	.7129	.4676	
					.7117	.4664	.60
16	1	3.0380	190.88	7.799	.4238	.3753	.59
					.4254	.3737	.82
					.4252	.3751	.83
17	2	4.3880	184.74	7.807	.7321	.4891	.84
					.7321	.4891	.84
17	1	3.0385	184.74	7.807	4	.3906	.84
					.4446	.3944	.87

TABLE IV

No. of alloy	Composition by volume, %	Density (obs.)	Density (calcd.)	β X 10⁶ (obs.)	β X 10⁶ (calcd.)	% Decrease in compressibility
1	55 Cu; 44 Ni; 1 Mn	8.910	8.901	0.62	0.64	3
2	33.7 Ni; 65.6 Fe; 0.7 Mn	8.402	8.206	.85		
3	78.4 Cu; 21.6 Al	7.847	7.582	.78	.89	12
4	66.9 Cu; 33.1 Al	7.244	6.870	.79	.98	19
5	75.5 Cu; 21.5 Zn	8.669	8.545	.75	.94	20
6	59.0 Cu; 41.0 Zn	8.426	8.200	.80	1.13	29
7	45.8 Cu; 54.2 Zn	8.291	7.960	.93	1.26	26
8	86.3 Cu; 13.7 Sn	8.631	8.710	.84	0.89	6
9	56.3 Cu; 43.7 Sn	9.024	8.210	.98	1.23	20
10	62.8 Cu; 37.2 Sn	8.913	8.320	.89	1.17	24
11	81.7 Al; 18.3 Mg	2.553	2.474	1.55	1.68	8
12	Pure aluminum	2.702		1.40		
13	86.6 Cu; 13.4 Si	8.406	8.050	.97	0.65	—49
14		7.798		.61		
15		7.835		.61		
16		7.799		.83		
17		7.807		.85		

Experimental Results.—These are given in Tables II, III and IV, together with other data necessary to the calculation of compressibility.

The compressibility coefficients represent the average compressibility between 100 and 500 megabars. The densities were determined on the bars upon which the compressibility measurements were made and serve as a valuable criterion of the solidity of the samples. It is, of course, essential for this work that the bars be free from voids. The anomalous density found for the copper-silicon alloy seemed to indicate the presence of voids and the excessively high value found for the compressibility also suggested this. In order to eliminate this possible source of confusion five of the alloy bars were subjected to x-ray inspection (numbers 2, 3, 6, 8 and 13) while immersed in methyl iodide. Four of the bars were found to be wholly free from voids, but the copper-silicon alloy was found to be very faulty, the x-ray photograph revealing casting pipe-cones throughout its length. The results on this alloy have, therefore, been discarded.

The densities were determined by the usual water displacement method, using a tare with each weighing and making correction for displacement of air. The data are summarized in Table IV. The calculated densities and compressibilities are obtained from the volume percentage compositions given in the second column. The values for β are the average values from Table III.[26]

Discussion.—In the simplest metallic solid solution, that is, of two metals crystallizing in the same crystal system (such as copper and nickel) and in which solid solution formation takes place by substitution of one atom of the solute for one atom of the solvent, the atoms are arranged crystallographically as they are in the pure component metals. As a consequence of the specific attraction between the unlike atoms (which may be taken as roughly indicated by the relative positions of the elements in the periodic table), the composite lattice will possess a rigidity greater than that of the component metals, in the same volume proportion, originating in the greater attractive (and repulsive) forces. Such a lattice will, therefore, have a smaller compressibility and the difference between the calculated and the observed compressibility coefficients will be indicative of the intensity of the attraction.

In the simplest case this should lead to an increase in density, and in general this is found to be the case, though the x-ray diffraction data on the copper–gold system indicate an exceptional behavior,[27] and a recent

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[26] Compressibility coefficients for the pure metals were taken from the data of Richards, THIS JOURNAL, **37,** **1646** (1915), except for aluminum, which was redetermined, and for nickel and copper (0.53 X 10^{-6} and 0.72 X 10^{-6}, respectively), which were calculated from Bridgman's data;[17] the densities of the pure metals are from the International Critical Tables, Vol. I, p. 103.

[27] Lange, *Ann. Physik,* **76,** 476 (1925), plotted *a*, the side of the unit face-centered cell, against atomic percentage composition and found a straight line relation within his experimental error. Kirchner, *Ann. Physik,* **69,** 59 (1922), found an increase in *a*, over the rule of mixtures value, with *a* plotted against atomic percentage composition,

study of the copper-rich copper-tin terminal solid solution is distinctly exceptional.[28] Davey[29] states that solid solutions of aluminum in silver, tin in silver and silicon in copper show in each case an increase in the dimensions of solvent lattice caused by the smaller solute atom. It is evident that it is questionable whether density is of any value as a criterion of the attraction between unlike atoms. Compressibility, however, is unaffected by this argument, since the forces effective in more tightly binding the atoms should also be effective in producing a diminished compressibility.

With respect to solid solutions of metals with different space lattices the foregoing argument requires some elaboration, as noted under the discussion of the experimental results on the various alloys of this type.

The specific attraction between the unlike atoms must be of immediate importance in the mechanical behavior of solid solutions. Solid solutions are much harder than required by the rule of mixtures, and a number of workers[30] have suggested that at least part of the increase in hardness must be caused by the attraction between unlike atoms. Hardness is a complicated property and each method of measurement brings the different factors concerned into play in varying degrees. Empirically it is defined as the resistance to permanent deformation. The tendency among metallurgists at present is to interpret this to mean resistance to slip along atomic planes.[31]

In solid solutions of normal grain size, free from foreign material of any kind and free from mechanical strain, the hardness must, by this theory, be caused only by the warping of the atomic planes, introducing resistance to slip, and by the attraction between the unlike atoms, tending to hold the lattice as a whole more rigid. Abnormally small grain size gives rise to a large increase in hardness, and mechanical strain, caused by cold-work

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amounting at the maximum to 0.9%, which is in excess of the probable experimental error. It is, however, not correct to plot a against atomic percentage composition, though this seems to be the general practice, for not a but a^3 is a linear function of atomic percentage composition when additivity is assumed. The correct procedure is to cube the values of a determined experimentally for the elementary metals, and by means of the atomic percentage composition calculate the values for a^3 for intermediate compositions and then to extract the cube root in order to obtain values for a truly representative of the rule of mixtures. Such a calculation for copper and gold will give a curve for a against atomic percentage composition slightly concave to the composition axis. Kirchner's data very nearly conform to this curve, falling at the greatest *0.5%* too high.

[28] Weiss, *Proc. Roy. Soc. (London),* ***108,*** *643* (1925), concluded from his x-ray data that this terminal solid solution is not of the simple substitutional type but that an atom of tin replaces several atoms of copper, leading to abnormally low densities.

[29] Davey, *Trans. Am. Soc. Steel Treating,* ***6,*** *375 (1924).*

[30] Desch, *Trans. Faraday Soc.,* ***10,*** *251 (1914).* See especially "Science of Metals," by Jeffries and Archer, McGraw-Hill Book Co., New York, *1924,* pp. *232, 260, 270, 396. 412.*

[31] The slip-resistance theory of hardness has been summarized by Jeffries and Archer, *Chem. Met. Eng.,* ***24,*** *1067 (1921).*

(plastic deformation), produces a similar result in smaller degree. It is the virtue of compressibility that it measures (in solid solutions) only one of these factors, namely, that caused by the attraction between unlike atoms. Bridgman[32] found that cold-rolled copper and iron gave the same values for compressibility as annealed copper and iron, within the accuracy of the measurements. This significant experiment demonstrates the essential identity of cold-worked and annealed metal, for an amorphous phase, in which the directional forces of the atoms producing the lattice characteristic of the metal are no longer nicely oriented with those of adjacent atoms or, in other words, in which the points of atomic attachment are no longer adjusted, should have a compressibility appreciably greater than that of the crystalline phase.[33]

In pure metals, which are mostly of high symmetry and free from the distortion solid solution formation produces, hardness is a periodic property[34] which, when compared to Richards' periodic curve of compressibility,[35] shows a striking and nearly perfect parallelism.[36] Exceptional metals are those of extraordinarily low symmetry.

Thus compressibility may be taken as a measure of the lattice rigidity factor in hardness. For solid solutions, the difference in compressibility of the solid solution and the value calculated on the basis of the rule of mixtures may be taken as a measure of the additional interatomic forces resulting from the chemical affinity operative between the unlike atoms, resulting in an increase in the lattice rigidity. Applied to alloys in this way, compressibility may be said to measure "chemical hardness." The other effects promoting slip resistance may be said to produce "physical

Without doubt the chemical factor is subordinate in magnitude to the physical, but the latter must be considered as intimately related to the chemical, for the warping of the atom planes, as a result of the introduction

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[32] (a) Bridgman, *Proc. Am. Acad. Arts Sci.*, 44, *265* (1909); (b) 58, 168 (1923).

[33] Bridgman's experiment (in which linear compressibility was measured) likewise points out the complete compressibility isotropy of these cubic lattices, for the process of cold-rolling inevitably produces preferred orientation. Similar experiments on a non-cubic metal, such as zinc, would, however, show nothing concerning the nature of cold-worked metal, since the preferred orientation produced by cold rolling would cause a very appreciable difference because of the well-known difference in compressibility along the different crystallographic axes.

[34] Rydberg, *Z. physik. Chem.*, 33, 353 (1900); Edwards, *J. Inst. Metals,* [2] *20,* **61** (1918).

[35] Ref. 26, p. 1643.

[36] Traube, Z. *anorg. Chem.*, 34, 413 (1903), pointed out the parallelism between hardness and internal pressure. This had been suggested (with the help of a few examples) by Richards in 1901. *Proc. Am. Acad. Arts Sci.*, **37**, 1 (1901).

[37] The value in the use of such terms is purely utilitarian: they serve to classify descriptively a series of facts or conditions producing a common effect.

of solute atoms, is caused by the difference in atomic volumes, modified in some way by the chemical attraction between the unlike atoms and the relative compressibilities of the partially ionized atoms.

System Copper–Nickel.—The only previous determination of an alloy in this system was made by **Grüneisen**,[22b] who determined E and a for a sample of commercial constantan. The compressibility coefficient calculated was **0.62** X 10^{-6}, agreeing with the value here determined.

The alloy measured was "Constantan," containing approximately **55%** copper, **44%** nickel, and **1%** manganese, by weight. No analysis was made of this alloy since the compressibility coefficients of these three metals are so nearly equal that only a very large departure from the reported composition could cause an appreciable variation in the calculated compressibility. The calculated compressibility was obtained from the value for nickel obtained by **Bridgman** expressed in terms of average compressibility between **100** and **500** megabars. namely, **0.53** X 10^{-6}.[38] The value **0.73** X 10^{-6} was taken as the most representative value for copper."[39] The calculated coefficient, **0.64** × 10^{-6}, is only very slightly greater than the observed value, **0.62** X 10^{-6}. The density increase, 0.1%, is also slight. Copper and nickel both crystallize in face-centered cubes. with approximately the same lattice constants, **3.597** and **3.499** **8..**respectively,@and are very similar chemically. No great decrease in compressibility is therefore to be expected.

System Iron–Nickel.—The only measurement made in this system was on a commercial alloy "Invar," received in the forged condition, containing 36.27% nickel. Filings of the alloy were examined by x-rays **for structure**, using the **Hull** powder method, and found to consist wholly of face-centered cubes, characteristic of nickel and **γ-iron**.[41] The compressibility coefficient found, **0.85** X 10^{-6}, is much higher than that calculated using the coefficient of a-iron (which is **0.60** X 10^{-6}), namely, 0.58 X 10^{-6}, and appears to mean that the **compressibility** of y-iron is much greater than that of **α-iron**.

System Copper–Aluminum.—Alloy **3** is in the a-field near the limit of solid solubility. Alloy **4** is a **β-solid** solution. There appears to be an appreciable increase in the cohesive forces in the b-solid solution, but a lower symmetry doubtless favors a **greater** hardness.

An accident prevented an investigation of annealed and age-hardened **duralumin**, but on **the** basis of the results presented here, especially those on steel, it may be predicted that the age-hardening, now known to be **produced** by the resistance to slip offered by submicroscopic particles of **$CuAl_2$** (in a pure copper-aluminum **alloy**)[42] will have only a very slight, probably inappreciable, effect upon the compressibility.

System Copper–Zinc.—A number of measurements have been reported on "brass," but with one exception there has been no accompanying analysis. Adams, Williamson and Johaston measured the compressibility of a leaded brass with **61.76%** copper. **35.92%** zinc, **2.26%** lead and **0.05%** iron. Their value (corrected) at zero pressure is **0.86** X 10^{-6}. For a brass of unstated composition **Madelung** and **Fuchs** found **0.90** X 10^{-6}

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[38] Richards' value for nickel, **0.43** × 10^{-6}, is apparently low.

[39] Bridgman's value (recalculated) is **0.730** X 10^{-6}, and the value **found** by Adams, Williamson and Johnston (corrected) is **0.725** X 10^{-6}. The above value is taken in preference to the slightly higher value of **0.75** X 10^{-6} given by Richards and **Grüneisen**.

[40] Davey, ***Phys. Rev.*, 25, 753 (1925).**

[41] This is in confirmation of the work of **McKeehan**, *Phys. Rev.*, **18, 657 (1921)**, and **Osawa**, **J.** Iron ***Steel Inst. London*,** May, **1926.**

[42] **Merica, Waltenberg** and Scott, ***Bull.*** Am. ***Inst. Min. Eng.*,** June, **1919**, p. **913.**

between 50 and 200 megabars. The other data appearing in the literature are of inferior accuracy, most of the values reported being higher than those obtained here. The higher value found by Adams, Williamson and Johnston may be explained in part by the lead present. The other higher values probably refer to copper-zinc alloys of higher zinc content.

Three compositions were investigated. An a-brass, half-saturated (18% zinc by weight), gave a compressibility of 0.75 X 10^{-6}, a decrease of 20% from the rule of mixtures value. An a-brass very near to the limit of solid solubility (35.6% zinc by weight), gave 0.80 $\times 10^{-6}$, a decrease of 29% from the rule of mixtures value. Despite this tremendous decrease, the hardness increase at the limit of solid solubility is only about 15%.[43] It is possible that this discrepancy is in some way related to the extraordinary elongation recently observed in a single crystal of α-brass,[44] a condition indicating, apparently, that certain of the factors which produce "physical hardness" in elementary zinc are no longer present when the zinc atom crystallizes on the copper lattice.

The decrease in compressibility is paralleled by an increase in density, which is 2.8% at the maximum.[45] In the elementary state the zinc is the more compressible element and it seems likely that the increase in density is taken up mostly by the zinc atoms, which on the copper lattice are forced out of their normal shape (that of a prolate spheroid) into approximately a sphere. The distance of closest approach of the zinc atoms in elementary zinc is 2.66 Å.,[46] whereas the distance of closest approach in copper is 2.56 Å.,[40] and the saturated solid solution 2.56 Å.,[47] so that the zinc atoms in a-brass are compressed on all sides, but mostly at the poles. It is possible that the zinc atom in brass is rotated in such a way that its major axis lies in the [111] direction in the copper lattice. If this were the case, a denser packing could result without any great compression of the zinc, assuming that the zinc atom lies wholly within the periphery of a prolate spheroid. Whether the copper atom is also compressed, as suggested by the increase in density, or expanded, as suggested by the apparent decrease in the cohesive forces (the compressibilities of the brasses are all less than that of pure copper, and it will be shown in a subsequent publication that the internal pressures are probably also less), appears at present to be beyond the reach of experiment.

The compressibility of the β-solid solution shows a decrease from the rule of mixtures value of 26%. The greater hardness of the β-solid solution is doubtless to be ascribed to a lower order of symmetry.[47]

System Copper–Tin.—The or-solid solution shows a compressibility slightly smaller than the rule of mixtures value, despite the fact that each tin atom replaces not one but several copper atoms.[28] Alloy 10, which is the δ-solid solution, appears to show a greater decrease than Alloy 9, the compound Cu_3Sn, and also exhibits a greater Brinell hardness,[48] though it is claimed that Cu_3Sn shows a greater scratch hardness.[49]

System Aluminum–Magnesium.—The composition investigated, 12.56% by weight of magnesium, is in the $a + \beta$ field[50] near the limit of solid solubility. The percentage decrease in compressibility observed, 8%, is relatively small, as is the percentage increase in density, which is 3%.

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[43] Harris, *J. Inst. Metals,* 28,327 (1922) states that the Brinell number of a 66–34 a-brass is 48. The Brinell number of pure copper is ordinarily taken as 40.

[44] Elam, *Proc. Roy. Soc. (London),* **115A,** 133 (1927).

[45] Jeffries and Archer, *Chem. Met. Eng.,* 29,925 (1923).

[46] Hull, *Phys. Rev.,* 17, 571 (1921).

[47] Ref. 4, p. 49.

[48] Bauer and Vollenbruck, *Z. Metallkunde,* 16,426 (1924).

[49] International Critical Tables, Vol. II, p. 561.

[50] Hanson and Gaylor, *J. Inst. Metals,* [2] 24,201 (1920).

Two determinations by other workers remain to be discussed. Bridgman[17] determined the linear compressibility at 30° of a piece of nichrome wire, approximating in composition to 80% nickel and 20% chromium by weight, or 76% nickel and 24% chromium by volume. Taking the compressibility coefficient of nickel from Bridgman's data, **0.53** X 10^{-6}, and that of chromium from Richards's data (after approximate conversion to Bridgman's units), **0.89** X 10^{-6}, the rule of mixtures value for this composition may be calculated to be **0.72 X** 10^{-6}. Bridgman found **0.55** X 10^{-6}, which is considerably lower.

Grüneisen's[22b] determination of the elastic constants for manganin leads to a compressibility coefficient of **0.81** X 10^{-6}. The calculated value for this alloy, assuming a composition of **82.1%** copper, **0.6%** iron, 15.0% manganese and 2.3% nickel, is **0.76** X 10^{-6}, appreciably lower than the determined value. There is some uncertainty concerning the composition of the alloy measured by Grüneisen (who gives no analysis), but the possible variation in composition from that assumed could hardly reconcile the calculated and the assumed values. It is the author's opinion that a direct measurement of the compressibility of thoroughly equilibrated manganin would show a compressibility coefficient only slightly different from the rule of mixtures value and that this difference would be negative, that is, that the coefficient calculated would be greater than that measured.

System Iron–Carbon.—The superior hardness of quenched steels has engaged the attention of metallurgists for many years. Although the problem is by no means solved, it is certain that the quenching hardness is related to the partially arrested transformation of austenite into pearlite and is directly caused by the constituent martensite. Most recent theories tautly assume that the hardness of martensite is chiefly the aforenamed "physical hardness," that is, it is caused by factors which impede slip without increasing the cohesive forces in the alloy.[51]

Most investigators of compressibility have made measurements on iron and steel but none seem to have investigated the special point of the effect of heat-treatment. The early values for the compressibility of iron were actually obtained from measurements on mild steel. Grüneisen,[22b] from measurements of the elastic moduli, calculated the compressibility of iron and of "steel," and found them to be the same, namely, **0.60** × 10^{-6}. Bridgman[52] measured the linear compressibility of Bessemer boiler plate and of annealed tool steel (1.25% carbon), and for the first found **0.530** X 10^{-6} (an average of two determinations, one made parallel to the direction of rolling and the other perpendicular to it) and for the second 0.525 **X** 10^{-6}. These figures are probably too low.[17]

Adams, Williamson and Johnston[n] measured the volume compressibility of Bessemer steel (**0.2%** carbon) and of tool steel (**0.8%** carbon), finding **0.575** X 10^{-6} for each. Madelung and Fuchs[18] found **0.61 X** 10^{-6} for both iron and steel ("silver steel").

The present work confirms previous work in the similarity of the compressibilities of annealed steel and iron, but gives a higher compressibility for hypereutectoid steel than would be expected from the measurements of Bridgman on annealed **1.25%** carbon steel.

In order to determine whether quenched steel possesses any superior cohesive forces, two sets of experiments were performed. A eutectoid steel (**0.89%** carbon) was quenched drastically (the heat treatments of these steels are given in Table I), a treatment which rendered it highly martensitic, and increased its hardness almost three-fold

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[51] Modern opinion on the nature of martensite and on the factors causing hardness in quenched steel has recently been summarized by Sauveur, Trans. Am. *Inst.* Mining Met. *Eng.,* No. 1532-C, 1926.

[52] **Ref.** 32 a, p. **255.**

(from a Brinell number, 3000 kg. load, of 241, to 653). The compressibility of this steel, an average of three determinations, was found to be 0.61 X 10^{-6}. The steel was then annealed thoroughly and its compressibility again determined, giving an average of three determinations, a value of 0.61 X 10^{-6}.

Similarly a hypereutectoid steel (1.36% carbon) was quenched as before and its compressibility found to be 0.83 X 10^{-6}, an average of three determinations. After annealing, the value found, an average of four determinations, was 0.85 × 10^{-6}, which within the possible error is identical with the first value.

It is therefore apparent that the hardening of steel by quenching is not caused by any appreciable increase in the normal cohesive forces, for the compressibility is not changed by quenching or annealing. It seems extraordinary indeed that a glass-hard steel should suffer the same volume decrease with increase in pressure as an annealed steel, but the result is not strange when examined in the light of the slip interference theory of hardness (with which it is in full accord), for this theory postulates no increase in the binding forces between the atoms in steel and assumes the hardness to be caused only by the mechanical arrangement of the structural units. It seems highly probable from the apparent identity of the compressibility values of the steels in the quenched and annealed conditions that the structural units in quenched steel are not greatly different from those in annealed steel, and this is in agreement with the explanation of the hardening of steel by the slip interference theory enunciated by Jeffries,[53] in which martensite is taken to be an aggregate of submicroscopic cementite and ferrite, differing from pearlite only in the size and arrangement of the cementite and ferrite grains.

Judging from Bridgman's experiment on rolled metals[32] neither variations in grain size nor mechanical strain appear to make any difference in compressibility (though it is conceivable that a decrease in density resulting from cold work or very small grain size should result in a slightly higher compressibility), so that an increase in hardness caused by either or both of these effects would make no difference in compressibility. On the other hand, lattice distortion, which has been postulated as a cause of hardness in steel, could be produced presumably only by an alteration in the interatomic forces, and this should result in an appreciable compressibility difference. The Hanemann-Schrader theory[54] assumes an ϵ- and an η-phase in equilibrium with austenite, and designates the η-phase as the bearer of the martensitic hardness because this phase is assumed to contain a hard iron carbide of the formula $Fe_{24}C$. It is assumed that the "hardness of martensite" is "caused by a definite arrangement of the iron and carbon atoms in an iron-carbon compound" ($Fe_{24}C$), and that this compound is hard because of the nature of its space lattice and because of the directional forces which inhere in the lattice. It is obvious that the compressibility results here presented limit the possible interpretations of this theory. The inherent hardness of the hypothetical compound $Fe_{24}C$, which is assumed to be much greater than that of ferrite or pearlite, must be explained either by (1) an extraordinarily low symmetry, or (2) interatomic forces between the iron and carbon atoms very much greater than those in austenite or pearlite, or by both (1) and (2). The assumption of the presence of large quantities of a compound of low symmetry seems to be untenable in the light of the results of x-ray diffraction studies on the structure of steel, for only the face-centered cube (characteristic of γ-iron) and the body-centered cube (characteristic of α-iron) have been found,[55] both lattices of high symmetry. The alternative (2) seems definitely denied by the compressibility measurements, which show no appreciable difference in the cohesive forces in quenched and an-

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[53] See Sauveur, ref. 51, p. 39.

[54] *Trans. Am. Soc. Steel Treat.*. 9,229 (1926).

[55] X-ray research on steel has recently been summarized by G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., New York, 1926, p. 210.

nealed steel. It is not impossible, of course, that there should be small quantities of a carbide such as $Fe_{24}C$ present in quenched steel, but the only large contribution such a compound could make to the superior hardness of martensite would be by virtue of a very fine state of subdivision. In such a form the Hanemann-Schrader is nearly indistinguishable from the more generally accepted slip-resistance theory, and in the assumption of the presence of an unknown compound of iron and carbon seems much less likely.

The compressibility of the eutectoid steel is only slightly higher than that of iron (0.61×10^{-6} and 0.60×10^{-6}, respectively), whereas the compressibility of the hypereutectoid steel is proportionately much greater (0.83×10^{-6}). The reason for this lack of proportionality is not now evident. The presence of voids in the hypereutectoid steel would of course account for the proportionately higher value, but this possibility is denied by the normal density (Table II). It is to be noted that though the compressibilities of eutectoid steel and of pure iron are nearly identical, the Brinell numbers are 241 and 75, respectively.

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Summary

1. The importance of a knowledge of the chemical affinity operative between unlike atoms in metallic solid solutions is emphasized. An attempt to measure the heat of formation of certain aluminum-magnesium and aluminum-zinc alloys is reported, in which the heat of solution of magnesium in $HCl.20H_2O$ is determined.

2. The compressibility of solid solutions is discussed and it is pointed out that in certain simple solid solutions the compressibility is a datum by which the intensity of the chemical affinity therein operative may be estimated.

3. Previous data on the compressibility of alloys are critically reviewed

and a series of new measurements on sixteen alloys, differing widely in type, is presented. It is shown that the greatest departure from simple additivity occurs in solid solutions of metals differing greatly in chemical type and that this departure is negative in every case under observation.

4. The basic importance of compressibility as a criterion of lattice rigidity in the study of the mechanical properties of metals and alloys, especially hardness, is emphasized, and the results of the compressibility measurements are correlated with the known mechanical properties and are interpreted to be in harmony with the slip-resistance theory of hardness. Measurements on quenched and annealed carbon steels are interpreted to indicate that the quenching hardness in these steels is not caused by an increase in the cohesive forces.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY AND THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

INTERNAL PRESSURES IN METALLIC SOLID SOLUTIONS

BY ROBERT FRANKLIN MEHL[1]

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The importance of compressibility in the study of chemical affinity in metallic solid solutions and intermetallic compounds has recently been emphasized, and it has been shown that from compressibility data interesting conclusions may be drawn concerning the metallurgical behavior of alloys.[2]

The problem of the attraction between unlike atoms in solid solutions may be attacked in a different way, namely, by the use of the concept of internal pressure. T. W. Richards,[3] and others,[4] have emphasized the importance of internal pressures among the factors which determine the existence and behavior of solids. Richards has correlated the conception with his equation of state for solids.[5,3a]

The quantity π_0, the internal pressure, was first calculated by the equation

$$\pi_0 = \frac{R}{V_A \alpha_s} \tag{1}$$

where V_A is the atomic volume, α_s the coefficient of cubic thermal expansion and R the gas constant. Richards recently modified this equation,[6] and now regards (1) as only an approximation. The new equation is

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[1] National Research Fellow.

[2] Mehl and Mair, THIS JOURNAL, 50, 55 (1928).

[3] The most recent treatment of internal pressures is given by (a) Richards, THIS JOURNAL, 48, 3063 (1926). The first of his many papers on this subject appeared in 1901; (b) *Proc. Amer. Acad. Arts Sci.*, *37*, *1* (1901).

[4] Traube, *Z. anorg. Chem.*, 34,413 (1903); Benedicks, *ibid.*, 47,455 (1905); Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, pp. 69, 185.

[5] Richards, THIS JOURNAL, 46, 1419 (1924).

[6] Ref. 3a. p. 3067.

$$\pi_0 = \frac{n'}{n' - m} \cdot \frac{R}{V_A\, \alpha_s} \tag{2}$$

n' and m are exponents in an abbreviated form of Richards's equation of state: $p + \pi_0 (V_0/V)^m = (\pi_p + P_\Theta)(V_0/V)^{n'}$, in which p is the external pressure. π_0 the intrinsic cohesive pressure, π_p the intrinsic distending pressure and P_Θ the thermal pressure. Using Equation (2) a series of values has been calculated for most of the cubic metals.

The simple structure of terminal solid solutions of cubic metals (of the simple substitutional type) immediately suggests that Equation (1) or (2) could be applied to estimate the chemical affinity between metals in the state of solid solution in terms of pressure, a step in the direction of evaluating this affinity in energy units. The data required are the mean atomic volume compressibilities and the coefficients of thermal expansion only, but it is necessary that the data for the pure component metals be known with an accuracy comparable with that for the alloys and also that these data refer to alloys of high purity. These two requirements appear to eliminate most of the current data on thermal expansion[7] with the exception of those on the copper-zinc system,[8] but the application of the internal pressure equation to this system is somewhat uncertain because zinc is not normally cubic. Richards prefers to limit the application of this form of his equation to cubic metals.

The recent work of C. H. Johansson,[9] however, on the thermal expansion of binary alloys of a series of cubic metals, is well adapted to the present purpose, especially since the crystal structure of each of the six systems investigated had been determined by x-ray diffraction studies which therefore give the necessary data on the mean atomic volumes.

Johansson measured the linear expansion of alloys in the systems: silver-palladium, copper-nickel, copper-gold, gold-palladium, copper-palladium and silver–gold. The coefficients at 35° are used in the calculation of the internal pressure. The datum desired is the increase in internal pressure over the rule of mixtures value for each composition. The atomic percentage composition of each alloy is required in order to calculate the mean atomic volume (which is a linear function of atomic composition when simple additivity is assumed), and the volume percentage composition in order to calculate the rule of mixtures coefficient of expansion. The cubic coefficient is obtained from the linear merely by multiplying by three; n' and m for each composition are calculated from the volume composition, since they are exponents of volume quantities. The rule of mixtures value for the internal pressure is calculated using Equation (2) and the rule of mixtures values for α_s and V_A; the "actual" internal pressure is calculated using Johansson's data (multiplied by three) and

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[7] Given in International Critical Tables, Vol. II, pp. 459–464.

[8] Hindert, Bureau of Standards, Scientific Paper, No. 410, 1922.

[9] Johansson, Ann. *Physik*, 76, 445 (1925).

the rule of mixtures value for V_A, corrected where necessary. The results of these calculations, as applied to several among the many compositions in each system investigated by Johansson, are given in Table I,

TABLE I

RESULTS OF CALCULATIONS

Atomic %	Volume %	a X 10⁶ at 35°	3α	Mean atomic volume	3α R. of M.	$\frac{n'}{n' - m}$	π_0 R. of M. kilomegabars	π_0 "actual" kilomegabars	Increase	% Increase
System Silver-Palladium (Compositions Refer to Palladium)										
0	0	19.05	57.15	10.28	57.2	1.42	199	199	..	0
8.9	7.8	17.9	53.7	10.16	55.5	1.42	206	214	8	3.9
30.6	27.6	15.5	46.5	9.85	51.3	1.42	230	254	24	10.4
50.9	47.3	14.0	42.0	9.57	47.0	1.42	259	290	31	12.0
65.7	62.4	12.55	37.65	9.37	43.8	1.42	284	330	46	16.2
86.4	84.6	12.55	37.65	9.08	39.0	1.42	332	341	9	2.7
100.0	100.0	11.9	35.7	8.89[a]	35.7	1.42	368	368	..	0
System Copper-Nickel (Compositions Refer to Nickel)										
0	0	16.9	50.7	7.12	50.7	1.55	352	352	..	0
9.8	9.1	16.0	48.0	7.07	49.6	1.55	363	357	12	3.3
30.1	28.5	15.2	45.6	6.96	47.4	1.55	386	401	15	3.9
50.1	48.2	14.4	43.2	6.86	45.1	1.55	411	429	18	4.4
69.6	67.9	13.95	41.85	6.75	42.8	1.55	440	450	10	2.3
94.8	94.4	13.05	39.15	6.62	39.7	1.55	484	491	7	1.4
100.0	100.0	(13.0)	39.0	6.59[b]	39.0	1.55	495	495	..	0
System Copper-Gold (Compositions Refer to Gold)										
0	0	16.9	50.7	7.12	50.7	1.55	352	352	..	0
20.9	27.5	15.6	46.8	7.77	48.6	1.44	314	326	12	3.8
30.0	38.0	15.15	45.45	8.05	47.9	1.40	298	315	17	5.7
45.0	54.0	15.0	45.0	8.52	46.7	1.36	281	292	11	3.9
69.2	76.3	14.8	44.4	9.26	45.0	1.32	260	264	4	1.5
83.8	88.1	14.55	43.65	9.72	44.1	1.30	249	252	3	1.2
100.0	100.0	14.4	43.2	10.22'	43.2	1.28	238	238	..	0
System Gold-Palladium (Compositions Refer to Palladium)										
0	0	14.4	43.2	10.22	43.2	1.28	238	238	..	0
18.6	16.6	13.0	39.0	9.99	43.0	1.30	254	274	20	7.8
40.1	36.8	12.2	36.4	9.73	40.4	1.32	276	306	30	10.9
49.8	46.3	11.9	35.7	9.60	39.7	1.33	286	319	33	11.5
61.1	57.7	11.9	35.7	9.45	38.9	1.35	302	328	26	8.6
74.7	72.0	11.9	35.7	9.26	37.8	1.37	322	341	19	5.9
100.0	100.0	11.9	35.7	8.89[d]	35.7	1.42	368	368	..	0
System Copper-Palladium (Compositions Refer to Palladium)										
0	0	16.9	50.7	7.12	50.7	1.55	352	352	..	0
19.4	23.1	14.95	44.85	7.46	47.2	1.53	357	375	18	5.0
36.4	41.7	13.6	40.8	7.76	44.5	1.49	355	386	31	8.7
49.8	55.3	12.85	38.55	8.00	42.5	1.47	356	392	36	9.9
59.3	64.5	12.45	37.35	8.17	41.0	1.46	358	393	35	9.8
78.4	81.9	12.05	36.15	8.51	38.4	1.44	362	385	23	6.4
100.0	100.0	11.9	35.7	8.89'	35.7	1.42	368	368	..	0

TABLE I (Concluded)

System Silver-Gold (Compositions Refer to Gold)

Atomic %	Volume %	$a \times 10^6$ at 35°	3α	Mean atomic volume	3α R. of M.	$\frac{n'}{n' - m}$	π_0 R. of M. kilomegabars	π_0 "actual" kilomegabars	Increase	% Increase
0	0	19.0	57.0	10.28	57.0	1.42	199	199	..	0
30.0	30.0	17.35	52.05	10.23	52.9	1.37	207	211	4	1.9
50.0	50.0	16.5	49.5	10.23	50.1	1.34	214	217	3	1.4
70.0	70.0	15.6	46.8	10.23	47.3	1.33	221	224	3	1.3
100.0	100.0	14.4	43.2	10.22[f]	43.2	1.28	238	238	..	0

[a] McKeehan, *Phys. Rev.*, 20, 428 (1922), found the lattice constants in this series of alloys to be very closely given by the rule of mixtures.

[b] Lange, Ann. *Physik*, 76, 476 (1925), found the lattice constants to be given within the possible experimental error by the rule of mixtures.

[c] The x-ray data on the crystal structure of this system are conflicting, as pointed out in a previous paper (ref. 2). It seems advisable to assume a simple additivity as best representative of the available data.

[d] Holgersson and Sedstrom, Ann. *Physik*, 75, 154 (1924), found the lattice constant in this series to deviate from the rule of mixtures value at the greatest by 0.6%, falling slightly below it. This variation is probably within the limit of accuracy of the measurements of the coefficient of thermal expansion and no correction need be made for it.

[e] Holgersson and Sedstrom, Ann. *Physik*, 75, 160 (1924), give values for the lattice constant which vary slightly above and below the rule of mixtures values. In general the intermediate compositions give values for a somewhat too low, but the irregularity of these values probably indicates a close adherence to the rule of mixtures. One alloy (45.5 atomic % palladium) gave evidence of the cesium chloride structure, rather than the face-centered cubic.

[f] Irregular results have been obtained for the lattice constants in this series by McKeehan, *Phys. Rev.*, 20, 428 (1922), who found *a* to depart from the rule of mixtures 1% at the maximum. On the other hand, Weiss, Proc. *Roy. Soc.* (London), 108, 643 (1925), found a strictly linear relation. Simple additivity of the atomic volume is assumed in the above calculations.

Copper and nickel are very similar chemically and have atomic volumes that are not greatly different, and the same is true of gold and silver. Accordingly there is little increase in π_0 over the rule of mixtures value (4 and 2%, respectively, at the maximum). Copper and gold are also very similar chemically, though the tendency to form compounds which they manifest in the solid state is reflected in the somewhat greater increase in π_0, though the difference in atomic volumes may also be contributory. The greatest increase in π_0 comes in the system silver-palladium (16%), elements adjacent in the periodic table. Then in order come gold-palladium (12%) and copper-palladium (10%).

It is to be noted that the increase in π_0 is apparently independent of the relative values for the component metals and independent of the difference in the lattice constants (and therefore the atomic volumes) of the component metals. With respect to the lattice constants, copper and gold differ by 0.468 Å. and give a $\Delta\pi_{\max.}$ value of 6%, whereas nickel and copper differ by 0.098 Å. and give a $\Delta\pi_{\text{max.}}$ value of 4%, and silver and palladium differ by **0.220** Å. and give a $\Delta\pi_{\text{max.}}$ value of 16%.[10]

The results are especially interesting in connection with the mechanical properties of solid solutions. Internal pressures are closely parallel to hardness for the pure metals and may be taken as an index of the lattice rigidity factor in hardness as distinguished from those factors which induce hardness by reason of lattice dissymmetry.[2] The percentage increase in internal pressure in a series of solid solutions may be compared with the percentage increase in hardness, and the magnitudes of these should give an analysis of the "chemical" and the "physical" factors in determining the hardness of solid solutions.[11]

High-grade hardness data are not available for all of the systems investigated by Johansson, but for the systems copper-nickel, silver-gold and gold-copper excellent data on the scratch hardness have been published by Kurnakov and Zemczuzny.[12]

Fig. 1 gives the percentage increase in π_0 and in the scratch hardness, plotted against volume percentage composition for the system silver-gold. At the maximum these are, respectively, 2 and 104%. If, therefore, the internal pressure and hardness be taken as directly proportional for the pure metals, it may be concluded that the hardest alloy in this series owes only about one-fiftieth of its hardness to the attraction between the unlike atoms.

A similar calculation for the copper-nickel system gives an increase of 4% in the internal pressures as compared to 63% in the hardness so that the "chemical hardness" in this system is 7% of the total hardness. In the copper-gold system these values are 6 and 100%, respectively, yielding a "chemical hardness" of 6% of the total.

The slip-resistance theory of hardness (in which hardness is defined as resistance to slip along atomic planes) recognizes two basic factors causing hardness in solid solutions.[13] These are (1) the attraction between unlike atoms and (2) crystalline dissymmetry caused by the warping of the atom planes with the introduction of the foreign atom. The calculations here presented are an attempt to evaluate the relative magnitudes of these two factors. In the nature of the case such an evaluation can only be semi-

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[10] The lattice constants for these metals are taken from Davey, *Phys. Rev.*, 25, 753 (1925).

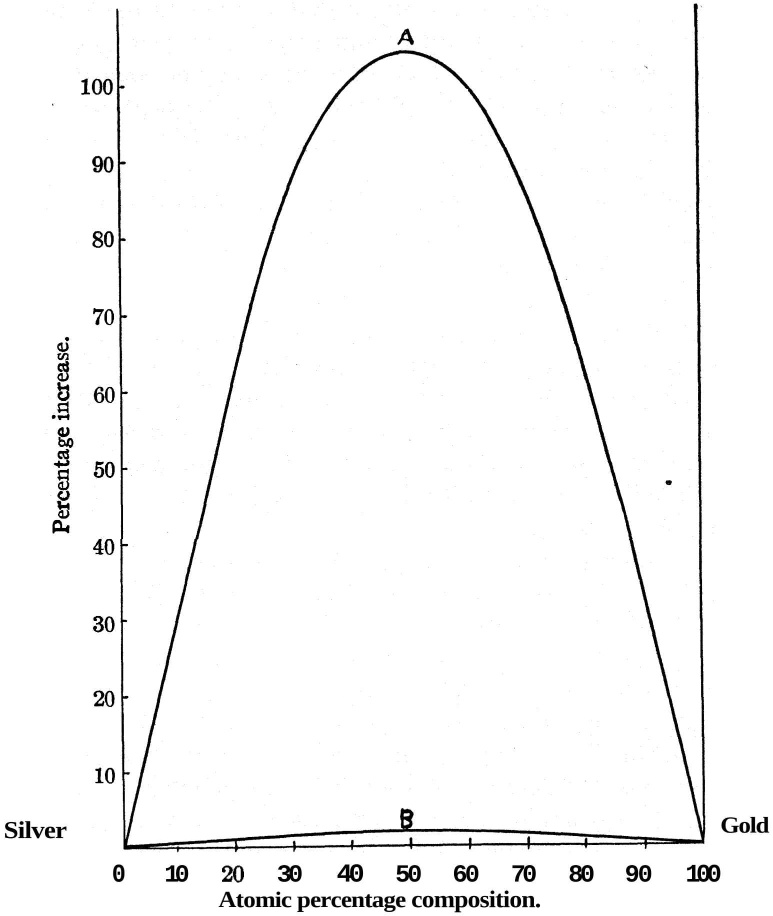
[11] Cold-work, which is very powerful in hardening metals and alloys, appears to have little or no effect upon the coefficient of thermal expansion [Jubitz, *Z. tech. Physik*, 7, 522 (1926)], and therefore upon the internal pressure calculated therefrom This emphasizes the fact that internal pressures are concerned only with purely cohesive forces and are not affected by lattice distortion or grain-size differences. It has already been pointed out (ref. 2) that compressibility is similarly unaffected by cold-work.

[12] Kurnakov and Zemczuzny, *Z. anorg. Chem.*, 54, 164 (1907); 60, 16 (1908).

[13] Jeffries and Archer, *Chem. Met. Eng.*, *24*, 1057 (1921).

quantitative, so that the percentages given must be regarded only as approximations.

Norbury[14] made measurements of hardness on a series of a-solid solutions of copper, and concluded that the hardening power of a solute atom is proportional to the difference in atomic volumes of the solute and the solvent. Rosenhain[15] has concluded that the hardness of solid solutions is largely caused by the lattice distortion introduced by the difference in size of the solvent and solute atoms. It is clear from the foregoing that Norbury's conclusion concerning the a-solid solutions of copper cannot be applied to the system silver-gold, nor perhaps to nickel-copper,



Curve A, hardness; Curve B, internal pressure.

Fig. 1

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[14] Norbury, Trans. *Faraday Soc.*, 19, 586 (1923-1924).

[15] Rosenhain, *Chem. Met. Eng.*, 28, 442 (1923).

for though the atomic volumes are nearly identical in each metal pair (10.28 and 10.22, and 7.12 and 6.59, respectively), the hardness reaches a maximum increase of 100.4% in the first and 63% in the second. The conclusion seems inescapable that the hardness in these solid solutions is not caused simply by the difference in sizes of the unlike atoms. In fact, if it be assumed that the internal pressures calculated in Table I apply to each separate atom it is clear that the atomic volumes of the atoms in solid solution cannot be the same as in the elementary state. In the silver-gold system, with increasing percentage of gold, the internal pressure increases from 199 kilomegabars for pure silver to 238 kilomegabars for pure gold, an increase of 39 kilomegabars. Obviously a pressure increase of such a magnitude would diminish the volume of the silver atom very appreciably. Conversely, in an alloy rich in silver, the gold atom, subjected to a smaller internal pressure than in the pure state, would increase in volume. This variation in volume would produce a slip-resistance not indicated by the relative atomic volumes of the metals in the pure state. It is not possible to calculate this volume change from the compressibilities of the pure metals, for even if the extrapolation to these high pressures and the approximation of the expansibility of the atom under an internal pressure decrease, be admitted, it must be remembered that because of the chemical attraction between the unlike atoms in the solid solution each atom is very probably partially ionized, and that .the ordinary compressibility coefficients are not applicable to the metal atom in this state. It is a significant fact, however, that the lattices of these solid solutions possess a high degree of symmetry, as shown by the sharpness of the reflection spectra obtained with x-rays. Whatever the volume changes suffered by the atoms, their symmetrical lattice positions must be accounted for, and the net volume change must be in accord with the observed small deviations from the rule of mixtures values for the densities.

As applied to non-cubic metals, the internal pressures calculated from the coefficient of linear expansion and the mean atomic volume may be taken to represent an *average* pressure around the periphery of the atom,[16] and accepting this extension of the foregoing argument, some interesting analogies can be drawn for the α-copper-zinc solid solutions.

Reference has already been made to coefficients of expansion for copper and the α-brasses.[8] There appears to be no satisfactory measurement for the coefficient of volume expansion for zinc at a comparable temperature but the linear coefficients determined by Bridgman[17] parallel and perpendicular to the hexagonal axis may be combined into a volume coefficient,

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[16] Richards, publication in press in J. *chim. phys.* See also THIS JOURNAL, 47, 732 (1925).

[17] Bridgman, *Proc. Am. Acad. Arts. Sci.*, *60*, *305* (1925).

namely, 82.6×10^{-6}.[18] Table II gives the results of these calculations, using Equation (1). All coefficients of thermal expansion are calculated to 20°.

TABLE II

RESULTS OF CALCULATIONS

Weight % of copper	Atomic % of copper	$a \times 10^6$	$3a \times 10^6$	Mean atomic vol., calcd.	Mean atomic vol., obs.	3α R. of M.	π_0 R. of M., kilomeg.	π_0 "actual." kilomeg.	Increase	% Increase
100.0	100.0	16.26	48.7	7.12	7.12	48.7	237[a]	237	..	..
90.3	88.1	17.02	51.1	7.32	7.24	52.7	213	222	9	4.2
80.0	76.3	17.23	51.7	7.52	7.36	56.7	193	216	23	11.9
75.3	70.9	17.59	52.8	7.61	7.44	58.6	184	209	25	13.6
70.3	65.4	17.77	53.3	7.71	7.51	60.4	176	205	29	16.5
0.0	0.0	...	82.6	9.16	9.16	82.6	109	109	..	..

[a] This value for copper differs from that given in Table I since the coefficient $n'/(n' - m)$ has been dropped. This coefficient is unknown for zinc, but its elimination can have only a very slight effect upon the figures in the last column.

This increase in internal pressure runs closely parallel with the related properties, as shown by Table III.

TABLE III

Weight % of copper	% Decrease in specific volume[a]	% Decrease in compressibility	% Increase in internal pressure
100.0	..	..	..
90.0	1.05	13	4.2
80.0	1.71	21	11.9
70.0	2.49	26	16.5
63.0	2.95	30	20.0

[a] The figures in the second column have been calculated from those cited by Jeffries and Archer, *Chem. Met. Eng.*, **29**, 925 (1923). Those in the third column are approximated from the values determined by the author in collaboration with B. J. Mair (ref. 2). Each column refers to the percentage change from the rule of mixture value.

A fifth column, giving the percentage increase in hardness, could be appended to this table, but this had not been done because of the disagreement among the various investigators concerning the hardness of the α-brasses.[19] However, the greater hardness of the a-brasses is clearly influenced by the chemical attraction between unlike atoms and the resultant denser packing, as illustrated by the last three columns in Table III. The probable effect

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[18] Bridgman's linear coefficients are, respectively, 57.4×10^{-6} and 12.6×10^{-6}. The volume coefficient is therefore $2\ (12.6 \times 10^{-6}) + 57.4 \times 10^{-6}$.

[19] Harris, *J. Inst. Metals*, **28**, 327 (1922), reported in International Critical Tables, Volume II, p. 555, finds that the Brinell numbers for a-brass with 90, 80 and 70 percentage copper by weight are identical, namely, 45, whereas that for the 66% copper alloy is 48. Taking 40 as the Brinell number for pure copper and 39 for zinc, this is an increase over the rule of mixtures value of only 20%. Jeffries and Archer, *Chem. Met. Eng.*, **29**, 967 (1923), state that the Brinell number rises from 35 for pure copper to 55 for a 70–30 brass, an increase over the rule of mixtures value of approximately 53%.

upon the zinc atom of this denser packing on the copper lattice has been discussed in a previous publication.[2]

Summary

1. It is pointed out that the chemical attraction between unlike atoms in metallic solid solutions of the simple substitutional type should manifest itself by increased internal pressures.

2. The average internal pressures in a series of binary systems of cubic metals have been calculated and it has been shown that the increase in internal pressure is positive and that it may amount to as much as 46 kilomegabars (in the silver-palladium system).

3. The results of the calculations of internal pressure have been applied in an analysis of the factors controlling hardness in solid solutions and it has been shown that the increased cohesive forces account for only a small fraction of the total hardness increase.

4. Similar calculations have been applied to the copper-zinc system, with limiting assumptions, and various properties affected by the increase in internal pressure have been correlated.

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 155]

THE ACID-FORMING PROPERTIES OF OSMIUM TETROXIDE

BY DON M. YOST AND ROBERT J. WHITE

RECEIVED OCTOBER 8, 1927 PUBLISHED JANUARY 5, 1928

Introduction

There has been difference of opinion as to whether osmium tetroxide, OsO_4, is an acid anhydride. Ephraim[1] concludes that the oxide probably does not form an acid from the supposed facts that its solubility in solutions of strong bases is the same as in water, that it does not react with them to form salts and that the concentration of hydroxide ion does not change when the tetroxide is dissolved in alkaline solutions. He did not regard as conclusive the evidence afforded by the results of Tschugaeff,[2] who prepared substances of the type $OsO_4.CsOH$ and $OsO_4.2KOH$. Since then Krauss and Wilkins[3] have also prepared unstable substances such as $OsO_4.2CsOH$. Hofmann[4] measured the electrical conductivity of osmium tetroxide solutions and found it to be very small; thus, with **1 g.** dissolved in **100** cc. of water the specific conductivity was found to be 10.9×10^{-6}, while that of the water used was 5×10^{-6}. He concludes that solutions of the

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[1] F. Ephraim, "Inorganic Chemistry," English translation by P. C. L. Thorne, Gurney and Jackson, London, 1926, p. 376.

[2] Tschugaeff, *Compt. rend.*, 167, 162 (1918).

[3] Krauss and Wilkins, Z. *anorg. allgem. Chem.*, 145, 151 (1925).

[4] Hofmann, Ehrhart and Schneider, *Ber.*, 46, 1657 (1913).

tetroxide are neutral and not acid. The qualitative experiments of von Wartenberg[5] constitute good evidence that the substance is an acid anhydride. He found that, while it could be almost completely extracted from its solutions in water by a few shakings with carbon tetrachloride, it could in turn be extracted almost completely from the carbon tetrachloride by four treatments with a 25% solution of sodium hydroxide. Finally, Professor W. C. Bray has pointed out to us that, inasmuch as the solutions of the tetroxide in water are nearly colorless while those in alkaline solutions are orange-yellow, a new substance must have been formed, which is probably an anion of the acid[6] H_2OsO_5.

This article describes an investigation of the distribution-ratios of osmium tetroxide between carbon tetrachloride and water and sodium hydroxide solutions, from which an ionization constant of perperosmic acid H_2OsO_5 has been calculated. Experiments with potassium chlorate solutions were also made to determine by an independent method whether or not osmium tetroxide forms a complex with chlorate ion; for Hofmann[4] found that the solubility of potassium chlorate is greater in solutions of the tetroxide than in water, and from these results concluded that a complex exists.

We wish to express here our appreciation of the helpful suggestions made by Professor A. A, Noyes. The investigation was aided on the financial side from a grant made to him by the Carnegie Institution of Washington,

Experimental Procedure

The water and carbon tetrachloride used in the experiments were freed from oxidizable impurities by well-known methods.

To a definite volume of the stock solution of osmium tetroxide in well-cleaned, glass-stoppered tubes definite volumes of water or solutions were added in amounts sufficient to make the total volume 25.00 cc. To this 25.00 cc. of carbon tetrachloride was added, the glass stoppers were inserted, the tubes placed in a thermostat at 25°, and shaken vigorously at frequent intervals. It was found that equilibrium was easily attained.

The method of analysis used was substantially that described by Krauss

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[5] Von Wartenberg, Ann., 440, 97 (1924).

[6] The naming of this acid offers special difficulty. It is highly desirable that the analogous acids of the elements manganese, iron, ruthenium and osmium have corresponding names. The acids H_2MnO_4, H_2FeO_4, H_2RuO_4, H_2OsO_4 are universally called manganic, ferric, ruthenic and osmic acids; and there exists an acid $HRuO_4$ which, in analogy with permanganic acid, is called perruthenic acid. This excludes the use of this name for the acid H_2RuO_5 (corresponding to RuO_4); and if the name perosmic acid be used, as it often is, for H_2OsO_5, it will introduce an inconsistency in the nomenclature of the related acids. A new type of name is therefore needed for the two acids of the elements with valence eight, and Professor A. A. Noyes has suggested to us that the most suggestive names would be derived by doubling the prefix *per*, thus designating H_2RuO_5 and H_2OsO_5 as perperruthenic and perperosmic acids.

and Wilkins.[3] It consisted in pipetting definite volumes of each liquid phase into 50 cc. of 2 N hydrochloric acid containing 2 g. of potassium iodide in stoppered flasks and titrating the liberated iodine with standard thiosulfate. Carbon tetrachloride was added to the mixtures in which it was not already present. It was necessary to extract the tetroxide from the chlorate solutions with carbon tetrachloride and analyze the extracts, since chloric acid reacts with iodide. The main objection to this method of analysis is the difficulty of determining the end-point in the dark green solutions of reduced osmium, especially when very dilute thiosulfate is used. The concentrations of thiosulfate varied from 0.00249 *N* to 0.0259 *N*, depending on the amount of osmium present in the sample analyzed.

Results of the Distribution Experiments

Table I contains the results. The distribution-ratios r are calculated directly from the concentrations by the expression $r = c_{\text{CCl}_4}/c_{\text{Aq}}$.

TABLE I

RESULTS OF THE DISTRIBUTION EXPERIMENTS AT 25°

Number	Millimoles of OsO_4 per liter in CCl_4 layer	Millimoles of OsO_4 per liter in Aqueous layer	Aqueous layer	Distribution-ratio r
1	6.40	0.532	Water	12.0
2	6.47	.545	Water	11.9
3	6.51	.541	Water	12.0
4	6.53	.532	Water	12.3
5	6.86	.558	Water	12.3
6	13.0	1.03	Water	12.7
7	13.1	1.02	Water	12.8
8	5.08	2.35	NaOH, 0.0587 N	2.16
9	5.09	2.36	NaOH, 0.0587 N	2.16
10	5.92	1.54	NaOH, 0.0277 *N*	3.84
11	5.92	1.54	NaOH, 0.0277 N	3.84
12	6.83	0.634	$KClO_3$, 0.2000 N	10.8
13	6.83	.632	$KClO_3$, 0.2000 N	10.7

The values of the distribution ratio between the tetrachloride and water show a slight increase with the concentration of the tetroxide, which is probably to be ascribed to error in the analyses of the more dilute solutions.

The Ionization Constant of Perperosmic Acid

We may assume that osmium tetroxide unites with water to form an acid which ionizes according to the equation $H_2OsO_5 = H^+ + HOsO_5^-$, and that correspondingly the reaction with hydroxide is $H_2OsO_5 + OH^- = HOsO_5^- + H_2O$. It is obvious then by the mass-action law, if K_w and K_A are the ionization constant of water and acid, respectively, that

$$\frac{(H^+)\,(HOsO_5^-)}{(H_2OsO_5)} = \frac{K_w(HOsO_5^-)}{(OH^-)\,(H_2OsO_5)} = K_A \qquad (1)$$

Now the quotient of the distribution ratio r_s for the alkaline solution and that, r_w, for water is evidently

$$\frac{r_s}{r_w} = \frac{(\mathrm{H_2OsO_5})}{(\mathrm{H_2OsO_5}) + (\mathrm{HOsO_5^-})} \text{ whence follows } \frac{(\mathrm{HOsO_5^-})}{(\mathrm{H_2OsO_5})} = \frac{r_w - r_s}{r_s}. \qquad (2)$$

Combining this with Equation (1) we get

$$K_A = \frac{K_w(r_w - r_s)}{(\mathrm{OH^-})r_s} \qquad (3)$$

The value of r_w is taken as 12.3, the average of experiments 1–7.

The values of K_A calculated with $K_w = 10^{-14}$ and r_s as given by experiments 8–9 and 10–11 are 8.0×10^{-13} and 7.9×10^{-13}, respectively. The agreement is very satisfactory.

This acid has therefore a constant even smaller than that of HCO_3^- (6×10^{-11}) and is one such that its salt $NaHOsO_5$ would be about 30% hydrolyzed in a 0.1 *M* solution. In view of the extreme weakness of the acid, it is not surprising that the tetroxide has not heretofore been proved to be an acid anhydride.

The results of experiments 12 and 13 show that a complex between osmium tetroxide and chlorate ion is probably formed, although it is not a very stable one.

Summary

The distribution ratio of osmium tetroxide between carbon tetrachloride and water has been found to have an average value of 12.3 when the concentrations are expressed in quantities per unit volume. The ratio is found to be much less when the aqueous phase consists of 0.0277–0.0587*N* sodium hydroxide, showing that much of the tetroxide is converted into a salt by the alkali. From the results, the ionization constant is calculated to be 8.0×10^{-13} for the first hydrogen of the acid H_2OsO_5, which it is proposed to call perperosmic acid.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE CATALYSIS OF ETHYL FORMATE BY MONOCHLORO-ACETIC ACID AND ETHYL ACETATE BY DICHLORO-ACETIC ACID IN NEUTRAL SALT SOLUTIONS

BY HERBERT S. HARNED AND J. ERSKINE HAWKINS

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With the exception of a few results obtained by Taylor[1] on the catalysis of ethyl acetate by dichloro-acetic acid and trichloro-acetic acid in potassium chloride solutions, few experimental data are available on ester hydrolysis by moderately strong acids in neutral salt solutions. To fill in this gap in the experimental material and to suggest a method of calculating the results are the objects of the present study.

Experimental Results

The usual method of titrating portions of the reaction mixtures with sodium hydroxide and barium hydroxide or with sodium hydroxide alone was employed. The unimolecular equation for the velocity was used. In the case of ethyl acetate hydrolysis, the variation of the velocity constants from the mean value during a given experiment was never greater than ±2% and was usually less than this amount. The calculation

TABLE I

MONOMOLECULAR VELOCITY CONSTANTS AT 25°

Part 1

Values of $k \times 10^4$

$CH_3COOC_2H_5$ (0.1 *N*)					0.202 *M* $CHCl_2COOH$		
Molal salt concn.	$BaCl_2$	NaCl	KCl	NaBr	KBr	$NaNO_3$	KNO_3
0.00	2.35	2.35	2.35	2.35	2.35	2.35	2.35
.25	2.98	2.74	2.66	2.66	..	2.65	2.37
.49	3.30	..	..	..	..	..	..
.50	..	2.88	2.70	2.80	2.56	2.71	2.36
.74	3.59	..	..	..	..	..	..
.75	..	..	..	..	..	2.74	2.40
.98	3.75	..	..	..	..	..	..
1.00	..	3.05	2.85	2.87	2.70	2.77	2.38
1.23	3.89	..	..	..	..	..	
1.48	4.03	..	..	..	..	..	
1.50	..	..	2.86	2.96	2.73	..	2.57
1.77	4.13	3.33	..	..	..	..	..
2.00	..	..	2.87	3.01	2.68	2.71	2.43
2.50	..	..	3.00	..	..	..	..
3.00	..	3.71	3.00	2.97	2.61	2.60	2.13
3.50	..	3.80	2.99	..	..	..	..
4.00	..	3.87	..	2.87	2.55	2.55	..
5.00	..	3.75	..	2.70	..	2.51	

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[1] Taylor, *Medd. Vetenskapsakad. Nobelinst.*, Vol. 2, No. 37 (1913).

TABLE I (Concluded)

Part 2

Molal salt concn.	$MgSO_4$	Na_2SO_4	K_2SO_4
0.000	2.35	2.35	2.35
.125	1.56	1.66	1.59
.250	1.49	1.37	1.28
.375	..	..	1.07
.500	1.39	1.16	1.02
.750	1.41	1.06	..
.875	..	1.07	..
1.000	1.44	1.04	..
1.250	1.52	1.01	..
1.500	..	1.06	..
2.000	2.00	..	..

Part 3

$HCOOC_2H_5$ (0.1 *N*)			0.287 M $CH_2ClCOOH$		
Molal salt concn.	NaCl	KCl	Molal salt concn.	Na_2SO_4	K_2SO_4
0.00	1.95	1.95	0.00	1.95	1.95
.50	2.52	2.11	.125	..	1.55
1.00	2.62	2.43	.25	1.67	1.44
1.50	2.77	2.44	.375	..	1.35
2.00	2.82	2.49	.50	1.53	1.28
2.50	2.89	2.43	.75	1.52	
3.50	..	2.25	1.00	1.61	
4.00	2.90		1.25	1.70	
5.00	2.84		1.50	1.50	..

of the results for the hydrolysis of ethyl formate showed some indication of autocatalysis. However, the results up to half decomposition of the ester showed little variation and their mean value was taken. In Table I the experimental results are given. All measurements were carried out at 25 ± 0.02°.

In Fig. 1 the velocity constants of the hydrolysis of ethyl acetate in the dichloro-acetic acid-salt solutions are plotted against the concentration of the added salt. Upon the first addition of the halides or sodium nitrate a very rapid increase in velocity constant occurs and as the salt concentration increases the velocity constant reaches a maximum and then decreases. No increase is observed in the case of potassium nitrate. With barium chloride the saturated solution is reached before a maximum occurs. Upon the addition of sulfates a rapid decrease in velocity constant is to be observed. As will be shown this is due to the removal of hydrogen ions to form HSO_4^-. In general this behavior parallels the neutral salt action on the velocity of hydrolysis of ethyl formate either in pure aqueous salt solutions or in salt solutions containing monochloro-acetic acid.[2,3]

[2] Manning, J. *Chem. Soc.*, 119,2079 (1921).

Warned, THIS JOURNAL, 49, 1 (1927).

Calculation of Results

(1) Halide Solutions

We may express the velocity of hydrolysis by the equation

$$v = k m_e m_{\mathrm{H}} F \qquad (1)$$

where m_e and m_{H} are the concentrations of the ester and hydrogen ion, respectively, and F is a kinetic factor which differs from unity because of the electrical field effects caused by the presence of the ions. If F equals $\gamma_e \gamma_{\mathrm{H}}$, the activity rate theory results, and if F equals $\gamma_e \gamma_{\mathrm{H}}/\gamma_i$, we obtain the equation of Brönsted.[4] γ_e, γ_{H} and γ_i are the activity coefficients of the ester, the hydrogen ion and the collision complex, respectively. In concentrated solutions and when dealing with reactions between ions and electrically neutral substances, recent experimental

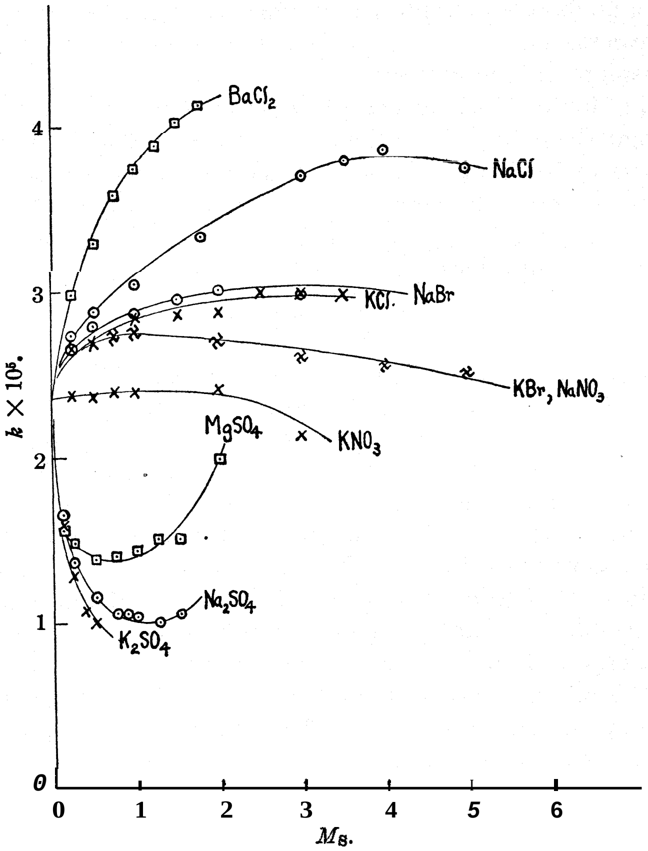

Fig. 1.—Velocity constants of hydrolysis of ethyl acetate by dichloro-aceticacid in salt solutions.

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[4] Brönsted, *Z. physik. Chem.*, 102, 169 (1922).

work seems to indicate that F is a more complicated factor than that given by either of the above theories. In any case thermodynamics demands that F be expressed, in part at least, in terms of the activity coefficients of the species present. In a recent investigation[3] of the autocatalysis of ethyl formate in aqueous neutral salt solutions, approximate results were obtained by making F unity. This, in these cases of ester hydrolysis, is not an exact procedure. Consequently, we have resorted to a method of computation by which the salt effect, F, is eliminated from the calculation.

Two assumptions are necessary:

(1) That hydrochloric acid at **0.1** M is completely dissociated.

(2) That the activity coefficients of the ester and ionic species are the same in the hydrochloric acid-salt solution containing the ester as in the dichloro-acetic acid-salt solution containing the ester at the same ionic strength.

Upon these assumptions, we find that

$$\frac{k_{\mathrm{HCl}}}{k_{\mathrm{di}}} = \frac{0.1}{m_{\mathrm{H}}} \tag{2}$$

where k_{HCl} is the velocity constant in the hydrochloric solutions and k_{di} is the velocity constant in the presence of the dichloro-acetic acid solutions.[5] In this way, the concentration of the hydrogen ion, m_{H}, in the dichloro-acetic acid solutions may be evaluated. The results of this calculation for potassium and sodium chloride and sodium bromide are given in Table II. Col. 1 contains the salt concentrations, m_{S}, Col. 2 the velocity constants of hydrolysis of ethyl acetate in **0.1** N hydrochloric acid solutions containing potassium chloride and sodium chloride taken from the results of Harned,[6] and sodium bromide from the results of Bowe.[7] Col. **3** contains the velocity constants read off from the curves of the data in Table I. Col. 4 contains the values of the hydrogen-ion concentration computed by Equation 2. The dissociation constant of dichloroacetic acid is given by

$$K = \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ac}}}{\gamma_{\mathrm{HAc}}}\frac{m_{\mathrm{H}}^2}{m_{\mathrm{HAc}}} = \gamma_{\mathrm{A}}\frac{m_{\mathrm{H}}^2}{m - m_{\mathrm{H}}} \tag{3}$$

By substituting **0.0816** for m_{H} and **0.202** for m, we obtain 5.53 X 10^{-2} for $\frac{m_{\mathrm{H}}^2}{m - m_{\mathrm{H}}}$, which agrees with the value 5.1 X 10^{-2} obtained from conductance data.[8] To evaluate K, we take γ_{A} to equal $\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}}$ or **0.60** at an ionic

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[5] This method of computing kinetic results has been employed by Bronsted and King, THIS JOURNAL, 47, 2523 (1925).

[6] Harned, *ibid.*, 40, 1461 (1918).

[7] Bowe, *J. Phys. Chem.*, 31, 290 (1927).

[8] Drucker, *Z. physik. Chem.*, 49, 563 (1904).

strength of 0.0816.[9] Hence K equals 3.32×10^{-2}. From this value of K, and from the values of m_H in Col. 4, γ_A for the salt solutions of different strengths was calculated by Equation 3. The results are given in Col. 5.

TABLE II

ACTIVITY COEFFICIENTS OF DICHLORO-ACETIC ACID IN SOME HALIDE SOLUTIONS

(1) Potassium Chloride

0.202 M $CHCl_2COOH$ $K = 3.32 \times 10^{-2}$

(1) m_s	(2) $k_{HCl} \times 10^5$	(3) $k_{di} \times 10^5$	(4) m_H	(5) γ_A
0.0	28.8	23.5	0.0816	0.600
.2	29.8	26.2	.0879	.490
.5	31.4	27.5	.0876	.495
1	34.1	28.6	.0839	.557
2	39.4	29.6	.0751	.747
3	44.6	29.2	.0655	1.056
(2) Sodium Chloride				
0.2	30.1	27.0	0.0897	0.463
.5	32.1	28.8	.0897	.463
1	35.7	30.7	.0860	.521
2	43.1	34.3	.0796	.647
3	52.3	37.1	.0709	.868
(3) Sodium Bromide				
0.2	29.7	26.2	0.0882	0.486
.5	30.9	27.7	.0896	.465
1	33.1	28.9	.0873	.500
2	37.4	30.0	.0802	.629
3	41.7	29.7	.0712	.857

The results for the monochloro-acetic acid hydrolysis of ethyl formate had to be calculated by a somewhat different method. Since no data are available on the hydrolysis of ethyl formate in hydrochloric acid-salt solutions, a direct determination of m_H by Equation 2 cannot be made. If we assume that the relative salt effect in this case is the same as in the case of ethyl acetate, then m_H may be evaluated by

$$\frac{k_{HCl}}{k_{mono}} = \frac{0.1\,R}{m_H} \qquad (4)$$

where R is a constant factor which relates the acetate with the formate hydrolysis. This was determined by calculating m_H in the 0.287 M monochloro-acetic acid solution. K was taken to be 4.2×10^{-3}, whence m_H equals 0.04 if γ_A is assigned the value 0.65 which is the ionic activity coefficient product of water at an ionic strength of 0.04.[10] Substituting

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[9] Harned, THIS JOURNAL, 47, 930 (1925).

[10] The value used for the dissociation constant is higher than the value, 1.6×10^{-3}, obtained by Ostwald, *Z. physik. Chem.*, 3, 170 (1889). Our justification for using 4.2×10^{-3} is the agreement obtained between γ_A for monochloro- and dichloro-acetic acids in a given salt solution at the lower concentrations.

the values of k_{HCl} and k_{di} in Equation (4), we obtain 0.591 for R. The values for γ_A in the salt solutions were then calculated by Equation (4). These are compiled in Table III.

TABLE III

THE ACTIVITY COEFFICIENTS OF MONOCHLORO-ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS

$CH_2ClCOOH$(0.287 *M*) $K = 4.2 \times 10^{-3}$ $R = 0.59$

Molal salt concn.	$k \times 10^5$	m_H	γ_A
		(1) KCl	
0.0	19.5	0.0400	0.65
.2	22.6	.0449	.50
.5	23.7	.0445	.51
1	24.2	.0420	.57
2	24.6	.0368	.76
3	24.2	.0321	1.05
		(2) NaCl	
0.2	23.3	0.0459	0.49
.5	25.1	.0463	.49
1	26.6	.0441	.52
2	28.4	.0390	.69
3	29.0	.0333	.96

The results of this calculation are given in Fig. 2. In the lower part, γ_A is plotted against $\mu^{1/2}$ where μ is the ionic strength. The solid lines and points are the values of the dichloro-acetic acid in the designated salt solutions, and the dotted lines represent the activity coefficients product of monochloro-acetic acid in potassium and sodium chloride solutions. In the upper part of the figure are the values of the activity coefficient product of water as determined by Harned[9] and Harned and James.[11] The inked-in circles in the lower part are the values of $\gamma_H\gamma_{OH}/a_{H_2O}$ in sodium chloride solutions. These are seen to agree very well with the values of γ_A of mono- and dichloro-acetic acid in the same salt solutions. It is also interesting to note that the order of the curves for $\gamma_H\gamma_{OH}/a_{H_2O}$ and γ_A in the three salt solutions are the same and their distribution similar. A better agreement is hardly to be expected and is a considerable improvement over the earlier calculations of Harned[8] on the neutral salt catalysis of ethyl formate in aqueous solutions.

(2) Sulfate Solutions

We attribute the decrease in velocity caused by the addition of sulfates to the formation of HSO_4^-. Since in these solutions the predominating influence is that of the removal of hydrogen ions, we may obtain an approximate solution by neglecting the salt effect, or by assuming that F in

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[11] Harned and James, *J. Phys. Chem.*, 30, 1060 (1926).

Equation (1) equals unity. Upon this assumption, the velocity constants will be proportional to the concentration of the hydrogen ion.

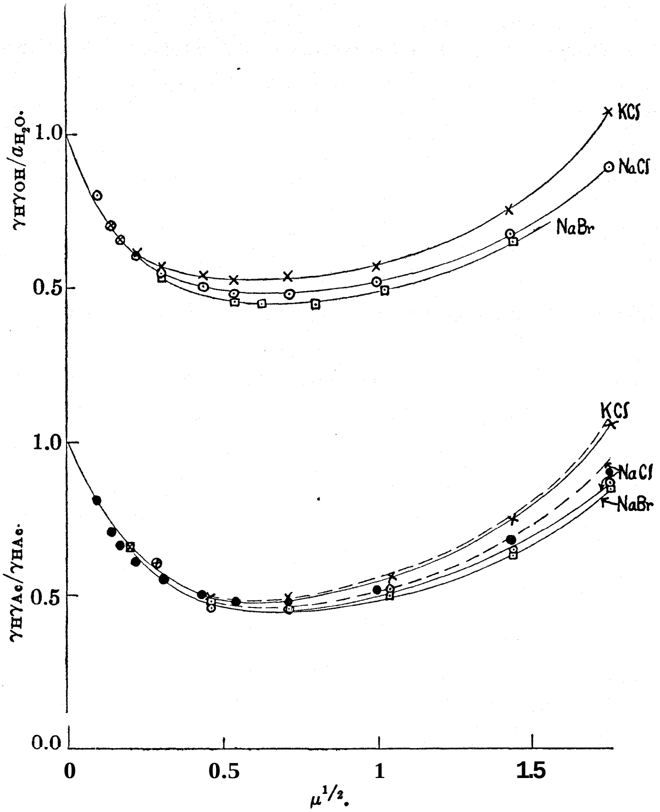

Fig. 2.—The activity coefficient products of mono- and dichloro-acetic acids in some halide solutions.

Let

$$\gamma_S = \frac{\gamma_H\gamma_{SO_4}}{\gamma_{HSO_4}};\quad \gamma_A = \frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}}$$

where the "γ's" are the activity coefficients of the species denoted by subscripts.

Let

M_{SO_4} = molal concentration of sulfate
M_{Ac} = molal concentration of dichloro-acetic acid
m_H = molal concentration of hydrogen ion
m_{Ac} = molal concentration of dichloro-acetate ion
m_{HSO_4} = molal concentration of HSO_4^-
m_{SO_4} = molal concentration of SO_4^{--}
m_{HAc} = molal concentration of undissociated dichloro-acetic acid molecules.

Then

$$\begin{cases} M_{\mathrm{Ac}} = m_{\mathrm{Ac}} + m_{\mathrm{HAc}} \\ M_{\mathrm{Ac}} = m_{\mathrm{H}} + m_{\mathrm{HSO_4}} + m_{\mathrm{HAc}} \\ M_{\mathrm{SO_4}} = m_{\mathrm{SO_4}} + m_{\mathrm{HSO_4}} \end{cases} \quad \text{or} \quad \begin{cases} m_{\mathrm{Ac}} = M_{\mathrm{Ac}} - m_{\mathrm{HAc}} \\ m_{\mathrm{HSO_4}} = M_{\mathrm{Ac}} - m_{\mathrm{H}} - m_{\mathrm{HAc}} \\ m_{\mathrm{SO_4}} = M_{\mathrm{SO_4}} - m_{\mathrm{HSO_4}} \end{cases} \tag{5}$$

In dilute solution, according to the theory of Debye and Hückel

$$\log \gamma_{\mathrm{S}} = -2\sqrt{\mu};\ \log \gamma_{\mathrm{A}} = -\sqrt{\mu}$$

and, therefore

$$\gamma_{\mathrm{S}} = \gamma_{\mathrm{A}}^2$$

Hence

$$K_1 = \gamma_{\mathrm{A}}^2 \frac{m_{\mathrm{H}}\, m_{\mathrm{SO_4}}}{m_{\mathrm{HSO_4}}} \tag{6}$$

$$K_2 = \gamma_{\mathrm{A}} \frac{m_{\mathrm{H}}\, m_{\mathrm{Ac}}}{m_{\mathrm{HAc}}} \tag{7}$$

Divide Equation (6) by the square of Equation (7) and obtain

$$\frac{K_1}{K_2^2} = \frac{m_{\mathrm{SO_4}}\, m_{\mathrm{HAc}}^2}{m_{\mathrm{H}}\, m_{\mathrm{HSO_4}}\, m_{\mathrm{Ac}}^2} \tag{8}$$

By substituting in the latter the values of the concentrations given in (5)

$$\frac{K_1}{K_2^2} = \frac{(M_{\mathrm{SO_4}} - M_{\mathrm{Ac}} + m_{\mathrm{H}} + m_{\mathrm{HAc}})\, m_{\mathrm{HAc}}^2}{m_{\mathrm{H}}\,(M_{\mathrm{Ac}} - m_{\mathrm{H}} - m_{\mathrm{HAc}})\,(M_{\mathrm{Ac}} - m_{\mathrm{HAc}})^2} \tag{9}$$

is obtained. By means of this equation m_{HAc} may be evaluated by arithmetical approximation since all other quantities are known. γ_{A} may then be determined by Equation (7) in the form

$$K_2 = \gamma_{\mathrm{A}} \frac{m_{\mathrm{H}}\,(M_{\mathrm{Ac}} - m_{\mathrm{HAc}})}{m_{\mathrm{HAc}}} \tag{10}$$

For K_2 we have taken the value previously employed, namely, 3.32×10^{-2} and for k, the value 1.15×10^{-2}.[12] The values for γ_{A} calculated by this method are given in Table IV.

Table IV

The Activity Coefficients of Dichloro-acetic Acid in Sulfate Solutions

(1) K_2SO_4

$M_{\mathrm{SO_4}}$	m_{H}	m_{HAc}	γ_{A}
0.0	0.0816	0.1204	0.600
.125	.0552	.0859	.445
.25	.0444	.0681	.380
.375	.0371	.0573	.354
.5	.0354	.0504	.311
	(2) Na_2SO_4		
0.125	0.0576	0.0855	0.422
.25	.0476	.0683	.356
.5	.0403	.0518	.284
.75	.0368	.0433	.246
.875	.0371	.0406	.223
1	.0361	.0384	.216
1.25	.0351	.0347	.196
1.5	.0368	.0327	.174

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[12] Noyes and Sherrill, This Journal, 48, 1861 (1926).

In Fig. 3 the values of γ_A in Table IV are plotted against the square root of the ionic strength. The values represented by triangles are the squares of the theoretical activity coefficients of a uni-univalent electrolyte computed by the Debye and Hückel equation

$$\log \gamma = -\frac{0.357\sqrt{2\mu}}{1 + A\sqrt{2\mu}}$$

where A represents the term containing the mean ionic diameters. A probable value of 0.8 was assigned to A. It is obvious that as μ decreases, the values of γ_A in these sulfate solutions approach the theoretical values.

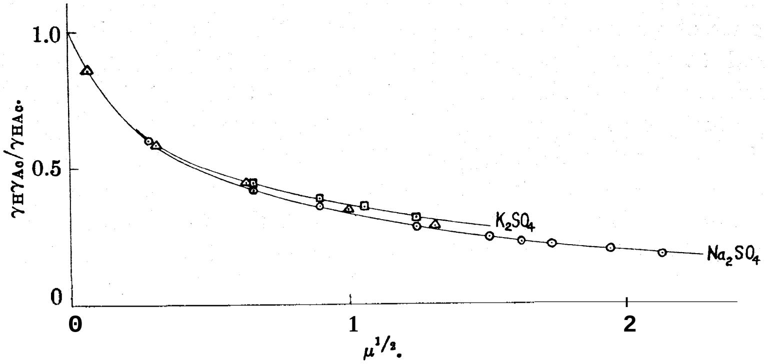

Fig. 3.—The activity coefficient product of dichloro-acetic acid in sulfate solutions.

Further, γ_A is greater in a potassium than a sodium sulfate solution of a given strength, a fact which agrees with the distribution of the ionic activity coefficient product of water as determined by Åkerlöf.[13]

Summary

(1) The velocity of hydrolysis of ethyl acetate at 25°, catalyzed by dichloro-acetic acid, has been determined in a number of salt solutions.

(2) Similar results have been obtained for the velocity of hydrolysis of ethyl formate, catalyzed by monochloro-acetic acid.

(3) A method of computing the activity coefficients of the acids from the kinetic data has been worked out and shown to yield reasonable results.

(4) An approximate method has been employed with success in computing the activity coefficients of the catalyzing acid in sulfate solutions. Although approximate, the method shows that the catalytic behavior in the sulfate solutions is largely determined by the formation of acid sulfate ions.

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[13] Åkerlöf, THIS JOURNAL, 48,1160 (1926).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. V THE ELECTRIC MOMENTS OF CERTAIN ORGANIC MOLECULES IN CARBON DISULFIDE AND HEXANE SOLUTION

BY JOHN WARREN WILLIAMS AND EARL F. OGG

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The utility of the Debye modification of the Clausius-Mossotti law for the calculation of the electric moments of certain molecules has been shown by several investigators.[1] At the present writing data for the moments of various types of organic molecules, calculated in the manner referred to above, are accumulating rapidly. In general, these figures are being obtained either from dielectric constant and density data for their solutions in benzene or from the temperature variation of the dielectric constant of their vapors. In this series of articles the dielectric constants of binary mixtures are being studied; therefore, it is concerned only with the first type of calculation, with the important modification, however, that other solvents besides benzene are being used. The third paper of this series[2] presented values for the electric moments of certain organic molecules, calculated from dielectric constant and density data of their solutions in carbon tetrachloride. The purpose of this paper is to show that carbon disulfide and hexane may also be used successfully as solvents for the purpose in hand. The electric moments of several organic molecules have been calculated from dielectric constant and density data in these solutions, data similar in all respects to those presented in previous papers of this series.

Method

The method used for the determinations of the dielectric constants of the solvents, carbon disulfide and hexane, and their solutions, was the electrical resonance method described in the first paper of the series.[3] The same frequency, 10^6 cycles per second, and the same temperature, 25°, were used for the measurements in every case.

Density determinations on the solutions were made at 25° using a 50cc. pycnometer of the Ostwald-Sprengel type. The usual precautions for precision work were observed throughout.

Purification of Materials

Carbon Disulfide.—The carbon disulfide was agitated with mercury to remove

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[1] (a) Lange, *Z. Physik*, 33, 169 (1925); (b) Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927); (c) Sanger, *Physik.* Z., 27, 556 (1926); (d) 28, 455 (1927); (e) Williams and Krchma, THIS JOURNAL, 49, 1676 (1927).

[2] Krchma and Williams, THIS JOURNAL. 49, 2408 (1927).

[3] Williams and Krchma. *ibid.*, 48, 1888 (1926).

foreign sulfides. It was dried by means of phosphorus pentoside, after which it was submitted to fractional distillation; boiling point 45.3–45.6°.

Hexane.—This liquid was obtained from the Eastman Kodak Company. It was thoroughly dried with phosphorus pentoxide and fractionally distilled; boiling point 67.5–70.5°. Owing to the difficulty of obtaining absolutely pure hexane, it was necessary to use the fraction as given. Since the material contained only saturated hydrocarbons, it served well as an electrically inert solvent.

Benzene.—The benzene was obtained in a thiophene free condition from the Eastman Kodak Company. It was dried and fractionated in the manner described by Richards and Shipley[4] and gave practically the same physical constants reported by these investigators.

Nitrobenzene.—The nitrobenzene used was obtained from the J. T. Baker Chemical Company. It was subjected to repeated fractional crystallizations and fractional distillations; boiling point 210.6–210.8°.

Chlorobenzene.—This material was obtained from the Eastman Kodak Company. It was carefully dried and fractionated; boiling point 130.7–131.0°.

Naphthalene.—Naphthalene, obtained from Merck and Company, was purified by crystallization and sublimation; melting point 80.1°.

Anthracene.—This material was purified by recrystallizing from toluene and washing with alcohol; melting point 217.6°.

Phenol.—Merck and Company "U. S. P.—C. P.—Loose Crystals" phenol was melted and fractionally distilled; boiling point 179.5–180.0°.

Benzoic Acid.—This material, obtained from the Mallinckrodt Chemical Company, was recrystallized from toluene and sublimed. The final product was in the form of pure white crystals; melting point 121.8'.

Cinnamic Acid.—Cinnamic acid, obtained from Kahlbaum, was purified by recrystallization from alcohol; melting point 132.6'.

Iodine.—The iodine, a Mallinckrodt product, was resublimed. It was used without further treatment.

Experimental Results

The results of the experimental work are presented in Tables I and II. In Table I dielectric constant and density data for solutions in carbon disulfide are given and in Table II similar data for solutions in hexane. The columns of these tables give, from left to right, the mole fraction of the solvent, in Table I, M. F. CS_2, in Table II, M. F. C_6H_{14}; the density of the solution compared to water at 25°, d_{25}^{25}; the observed dielectric constant of the solution, ϵ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2}\frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2$; and the molar polarization of the second component $P_2 = \frac{P_{1,2} - f_1P_1}{\mathrm{fa}}$. The dielectric constant data are accurate to within 0.1 of one per cent.

It will be noted that these data are somewhat different in certain respects. In the case of the binary liquid mixtures the two components are mutually soluble in all proportions, while in the case of the binary systems in which the solute is a solid substance, examples are presented

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[4] Richards and Shipley, This Journal, 41, 2822 (1919).

which show widely varying solubilities. The solubilities of the benzoic acid, cinnamic acid and anthracene in carbon disulfide and the solubility of the benzoic acid in hexane were so slight that the calculation of their molar polarizations was not attempted. However, their dielectric constant and density data have been included in the tables.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR SOLUTIONS IN CARBON DISULFIDE

M. F., CS$_2$	d^{25}_{25}	ϵ	$P_{1,2}$, cc.	P_2, cc.
		Carbon Disulfide—Benzene		
1.00	1.2598	2.633	21.26	29.0
0.75	1.1200	2.531	23.11	28.4
.50	1.0220	2.441	24.44	27.8
.25	0.9450	2.358	25.54	27.0
.0	.8746	2.285	26.66	26.7
		Carbon Disulfide—Hexane		
1.00	1.2598	2.633	21.26	31.6
0.75	1.0110	2.319	23.71	30.8
.50	0.8630	2.126	25.65	30.1
.25	.7550	2.003	27.68	29.6
.0	.6796	1.904	29.27	29.2
		Carbon Disulfide—Chlorobenzene		
1.00	1.2591	2.633	21.27	82.5
0.90	1.2320	3.087	26.54	75.4
.75	1.1988	3.627	33.12	68.2
.50	1.1572	4.449	43.52	66.4
.25	1.1276	5.094	52.91	63.3
.0	1.1011	5.610	61.81	62.0
		Carbon Disulfide—Nitrobenzene		
1.00	1.2591	2.633	21.26	346
0.95	1.2530	4.350	32.99	260
.90	1.2465	6.060	40.64	216
.75	1.2315	9.810	53.50	150
.50	1.2173	17.34	69.14	117
.25	1.2080	24.60	81.78	101
.0	1.2022	36.10	94.30	94
		Carbon Disulfide—Phenol		
1.000	1.2591	2.633	21.28	83.6
0.996	1.2578	2.644	21.44	83.6
.984	1.2544	2.714	22.11	83.6
.969	1.2500	2.794	22.94	83.6
.955	1.2464	2.868	23.63	83.6
.931	1.2394	3.040	25.21	83.6
.903	1.2320	3.246	27.04	83.6
		Carbon Disulfide—Naphthalene		
1.000	1.2591	2.633	21.27	54
0.999	1.258	2.641	21.37	54

TABLE I (*Concluded*)

M. EL, CS_2	d_{25}^{25}	ϵ	$P_{1,2}$, cc.	P_2, cc.
.994	1.255	2.646	21.55	54
.983	1.246	2.654	21.93	54
.973	1.240	2.663	22.25	54
.965	1.235	2.673	22.59	54
.935	1.225	2.680	23.30	54
Carbon Disulfide—Anthracene				
1.0000	1.2591	2.633	21.27	
.9998	1.2590	2.641	21.34	
.9996	1.2590	2.646	21.41	
.9992	1.2589	2.649	21.46	
.9984	1.2588	2.662	21.57	
.9981	1.2587	2.665	21.63	
.9957	1.2581	2.674	21.79	
Carbon Disulfide—Benzoic Acid				
1.0000	1.2591	2.633	21.28	
0.9998	1.2591	2.644	21.40	
.9992	1.2590	2.651	21.47	
.9985	1.2589	2.657	21.54	
.9970	1.2588	2.663	21.56	
.9947	1.2584	2.666	21.66	
.9924	1.2580	2.668	21.70	
Carbon Disulfide—Cinnamic Acid				
1.0000	1.2598	2.633	21.26	
0.9997	1.2594	2.645	21.39	
.9992	1.2592	2.649	21.45	
.9986	1.2586	2.663	21.55	
.9972	1.2583	2.673	21.70	
.9963	1.2581	2.679	21.76	
Carbon Disulfide—Iodine				
1.000	1.2591	2.633	21.27	60.3
0.995	1.2763	2.669	21.53	60.3
.993	1.2830	2.672	21.58	60.3
.990	1.2910	2.684	21.65	60.3
.987	1.3010	2.710	21.88	60.3
.983	1.3115	2.718	21.96	60.3

TABLE II

DIELECTRIC CONSTANT AND DENSITY DATA FOR SOLUTIONS IN HEXANE

Hexane—Benzene

M. P., C_6H_{14}	d_{25}^{25}	ϵ	$P_{1,2}$, cc.	P_2, cc.
1.00	0.6800	1.904	29.25	27.8
0.91	.695	1.931	29.11	27.6
.75	.717	1.981	28.84	27.4
.50	.757	2.054	28.20	27.0
.25	.810	2.160	27.49	26.8
.0	.875	2.283	26.65	26.7

TABLE II (Concluded)

M. F., C_6H_{14}	d^{25}_{25}	ϵ	$P_{1,2}$, cc.	P_2, cc.
		Hexane—Chlorobenzene		
1.00	0.680	1.904	29.25	84.0
0.90	.720	2.167	34.51	81.0
.75	.774	2.605	41.68	78.7
.50	.874	3.462	51.10	72.8
.25	.984	4.508	57.99	67.4
.0	1.104	5.610	61.70	61.7
		Hexane—Nitrobenzene		
1.00	0.680	1.904	29.25	346.0
0.95	.700	2.624	44.08	322.0
.90	.724	3.474	55.92	293.0
.75	.794	6.300	76.61	218.4
.51	.915	14.68	93.40	156.8
.0	1.202	36.10	94.32	94.3
		Hexane—Naphthalene		
1.000	0.6796	1.906	29.28	55.0
0.998	.6809	1.919	29.61	55.0
.987	.6849	1.928	29.85	55.0
.984	.6861	1.930	29.93	55.0
.977	.6885	1.936	29.97	65.0
.972	.6899	1.939	30.10	55.0
.964	.6920	1.941	30.13	55.0
		Hexane—Benzoic Acid		
1.0000	0.6796	1.904	29.26	
.9992	.6803	1.912	29.40	
.9980	.6810	1.915	29.51	
.9974	.6811	1.915	29.60	
.9964	.6812	1.916	29.62	
.9957	.6814	1.917	29.62	
.9950	.6817	1.918	29.66	
		Hexane—Carbon Disulfide		
1.00	0.6796	1.904	29.27	29.2
0.75	.7550	2.003	27.68	29.6
.50	.8630	2.126	25.65	30.1
.25	1.0110	2.319	23.71	30 8
.0	1.2598	2.633	21.26	31.6

Calculation of the Electric Moments of the Various Solute Molecules

The dielectric constant and density data using carbon disulfide and hexane as non-polar solvents for certain organic molecules are exactly similar to those obtained for the binary systems considered in the three preceding papers of this series,[1d,2,5] in which either benzene or carbon tetrachloride was used as the solvent. The calculations of the electric moments of the various solute molecules to be presented in this article

[5] Williams and Allgeier, THIS JOURNAL, 49, 2416 (1927).

were made in the same manner and making the same assumptions, so that the details will be omitted.

The electric moments of the various solute molecules, calculated from dielectric constant and density data of their solutions in carbon disulfide, are given in Table III. In Table IV are given the results of similar calculations for the electric moments of certain solute molecules from like data in hexane solutions. The symbols of the previous articles have been retained throughout.

TABLE III

ELECTRIC MOMENTS OF SOLUTE MOLECULES (CARBON DISULPIDE AS SOLVENT) AT 25°

	P''_2, cc.	P'_2, cc.	$\mu \times 10^{18}$
Phenol	27.5	56.1	1.63
Naphthalene	43.5	10.5	0.69
Benzene	25.8	2.7	0.09
Nitrobenzene	32	314	3.89
Chlorobenzene	31	61	1.52
Hexane	29.6	2	0.08

TABLE IV

ELECTRIC MOMENTS OF SOLUTE MOLECULES (HEXANE AS SOLVENT) AT 25°

	P''_2, cc.	P'_2, cc.	$\mu \times 10^{18}$
Carbon disulfide	21.1	2	0.08
Naphthalene	43.5	11.5	0.72
Benzene	25.8	2	0.08
Nitrobenzene	32	314	3.89
Chlorobenzene	31	53	1.55

It is of interest also to consider benzene as the solvent in the case of the systems carbon disulfide-benzene and hexane-benzene. This permits a calculation of the electric moments of the carbon disulfide and hexane molecules, the results of which are given in Table V.

TABLE V

ELECTRIC MOMENTS OF CARBON DISULPIDE AND HEXANE (BENZENE AS SOLVENT) AT 25°

	P^{a}_{2}, cc.	P'_2, cc.	$\mu \times 10^{18}$
Carbon disulfide	21.1	1.1	0.06
Hexane	29.6	0.9	0.05

Discussion of Tables of Electric Moments

One exceedingly important conclusion can now be drawn from the data made available by this series of articles, namely, that the value of the electric moment for the solute molecules, calculated from dielectric constant and density data in various non-polar solvents, is quite independent of the solvent used. This point is illustrated by the data collected in Table VI.

TABLE VI

ELECTRIC MOMENT DATA FOR CHLOROBENZENE AND NITROBENZENE IN VARIOUS SOLVENTS—TEMPERATURE, 25°

Solvent	e (solvent)	P_2 (C_6H_5Cl)	$\mu \times 10^{18}$ (C_6H_5Cl)	P_2 ($C_6H_5NO_2$)	$\mu \times 10^{18}$ ($C_6H_5NO_2$)
Carbon disulfide	2.633	82.5	1.55	346	3.89
Benzene	2.283	82	1.55	344[a]	3.84
Hexane	1.904	84	1.56	346	3.89

[a] The value for $P_2(C_6H_5NO_2)$ in benzene solution was taken from Miss Lange's work, Lange, *Z. Physik*, 33, 169 (1925). This value has recently been checked in the Wisconsin Laboratory by Mr. C. H. Schwingel in the course of an investigation of the dielectric properties of certain nitro derivatives of benzene and toluene in benzene solution, the results of which will be published shortly.

It might have been predicted that since the dielectric constant of the solvent changes, a change in the molar polarization of the solute molecule, and therefore in its electric moment, should result. Indeed it may be said that from the meager data available to the time of these researches slight differences were indicated in the molar polarization values depending on the non-polar solvent used. The present authors believe that for the first time sufficiently accurate data have been accumulated to prove that such is not the case.

The data of this article have been used to calculate the electric moments of the molecules of the solvent media and their values have been included in the tables. The moments for benzene, carbon disulfide and hexane are practically zero; in other words they are non-polar in nature. This fact permits their use as solvents in studies of the type previously referred to.[1] The value $\mu = 0.08 \times 10^{-18}$ for benzene is of interest in connection with the article of Sänger,[6] in which this author shows from dielectric constant data on pure benzene and certain theoretical considerations that this molecule should have practically a zero moment.

The value found for the electric moment of naphthalene, $\mu = 0.70 \times 10^{-18}$, is of special interest to the organic chemist. If the structural formula for the substance is written in the conventional way, there results a molecule which appears to be symmetrical, or in the terms used here, it would appear to have a zero moment. The result presented above is not surprising since it is well known that the second benzene ring of the naphthalene behaves quite differently chemically from the first. The data for anthracene indicate that it has a much higher molar polarization, and therefore a higher electric moment, than naphthalene.

Phenol dissolved in carbon disulfide gave a value of $\mu = 1.63 \times 10^{-18}$, in excellent agreement with that found in benzene solution,[5] $\mu = 1.70 \times 10^{-18}$.

The agreement between the values of the electric moments found for

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[6] Sänger, *Physik. Z.*, 27, 165 (1926).

chlorobenzene and nitrobenzene in the various solvents used leaves nothing to be desired. This agreement is shown amply in Table VI.

Summary

1. Using an electrical resonance method previously described, dielectric constant data have been obtained for carbon disulfide solutions of benzoic acid, phenol, cinnamic acid, iodine, naphthalene, anthracene, benzene, hexane, nitrobenzene and chlorobenzene, and for hexane solutions of benzoic acid, naphthalene, benzene, nitrobenzene and chlorobenzene, Corresponding density determinations have been made.

2. The data have been applied to the calculation of the electric moments of a majority of the solute molecules.

3. The data of this article prove that the molar polarization, and therefore the electric moment, of a solute molecule is independent of the non-polar solvent used.

4. The solvents benzene, carbon disulfide and hexane have been shown to be non-polar in character.

MADISON, WISCONSIN

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

THE ENTROPY OF HYDROGEN CHLORIDE. HEAT CAPACITY FROM 16°K. TO BOILING POINT. HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID

BY W. F. GIAUQUE AND R. WIEBE

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The results presented in this paper were obtained in the first of a series of researches on low temperature calorimetry of condensed gases. This research, which was started in 1922, is in active continuation. It is hoped that the more important substances of simple structure which are gases under ordinary conditions will be investigated, or perhaps we should say re-investigated since data exist in many cases. In addition to the data presented in this paper, measurements on hydrogen bromide and hydrogen iodide have been completed but will not be available until the completion of the laborious calculations.

Our immediate purpose is the testing of the third law of thermodynamics and more particularly the comparison of the entropy, as obtained from this law, with that obtained from various theories with the assistance of spectroscopic data It seems almost unnecessary to state that such a purpose imposes severe requirements on the accuracy of the measurements.

Hydrogen chloride was selected because of the reliability of band spectra measurements and their interpretation for this substance. While the measurements were in progress the results of a similar investigation by Eucken and Karwat[1] and by Karwat[2] appeared. However, our experimental data are in considerable disagreement with those of the above authors, thus necessitating a different conclusion as to the interpretation. This confirms our previous conclusion regarding the desirability of new determinations in other cases.

Preparation of Hydrogen Chloride.--The preparation of pure anhydrous hydrogen chloride in large quantities proved to be one of the most difficult parts of the work. The amount required to fill the calorimeter was about 3.5 moles, and it was necessary to work with as much as 10 moles to allow for losses during the purification. At first the gas was prepared by the addition of sulfuric acid to sodium chloride in a system which had been evacuated. The gas was further dried by passing through sulfuric acid and through phosphorus pentoxide before condensation in a bulb cooled with liquid air. C. P. reagents only were used. Hydrogen chloride prepared in this manner had two properties which required further investigation; first, the condensed material was of a reddish pink color; second, on melting it was obviously impure since solid white particles could be seen in the colorless liquid.

Pink Hydrogen Chloride.—The most obvious assumption would be that some impurity caused the pink color but additional experiments did not support this explanation. The reddish pink color was obtained only when the condensation by liquid air took place *in vacuo.* When hydrogen chloride was passed into a condensation bulb which contained air and was left open to the atmosphere, the crystalline material was white. When the liquid air was removed from a bulb containing pink crystals, thus allowing the temperature to rise, the pink color disappeared abruptly, leaving white crystals. This occurred at a temperature very little above that of liquid air, probably within 10 or 20 degrees above the boiling point. Subsequent cooling in liquid air did not restore the pink color. The intensity of the color varied with the conditions, a greater intensity resulting when the gas was more slowly admitted to the condensation bulb. The possible sources of impurity were the reagents and stopcock grease. Since other reagents could be used, the following methods of preparation were carried out with stopcocks in the system.

$NH_4Cl + H_2SO_4$,	HCl dried with H_2SO_4 and with P_2O_5
HCl (aq.) + H_2SO_4,	HCl dried with H_2SO_4 and with P_2O_5
$NH_4Cl + H_3PO_4$,	HCl dried with P_2O_5 only
$NaCl + H_2SO_4$,	HCl dried with H_2SO_4 only

C. P. phosphorus pentoxide was available from several sources, and samples from some lots turned brown on treatment with concentrated H_2SO_4. Such material was not used, and we believe that the phosphorus pentoxide which was used for preparation purposes was of the highest quality.

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[1] Eucken and Karwat, *Z. physik. Chem.*, 112, 467 (1924).

[2] Karwat, *ibid.*, 112, 486 (1924).

Pink hydrogen chloride was produced by each of the above methods, in one of which phosphorus pentoxide was carefully eliminated. Finally, a closed apparatus was constructed without stopcocks in which, after evacuation by a mercury diffusion pump and sealing off, sodium chloride and sulfuric acid could be mixed and the gas condensed in a bulb either after or before drying with phosphorus pentoxide. This also produced pink hydrogen chloride. One of the bulbs of this apparatus had purposely been made of thick glass with a thin spot on one side. It was found that in this case the material on the thin spot was pink while the remainder was white. This explains the effect produced by the presence of air, namely, that unless the inside wall of the vessel is kept practically at the temperature of liquid air the pink modification will not form. It was not possible to obtain the pink form in the calorimeter since the gas was necessarily liquefied first in the process of filling. There was a transition at 98.36°K. in the calorimeter but both forms are colorless, as could readily be observed by freezing the liquid and cooling the solid to about 83°K. in glass. It seems probable that the reddish pink material is an unstable crystalline form of hydrogen chloride. Since it was always mixed with some white material it may be presumed that the color of the pure unstable form would be considerably darker than the color observed. The existence of a third crystalline form is supported by the work of Simon and Simson,[3] who found by x-ray analysis that the form stable at the melting point had a face-centered cubic structure, while at the temperature of liquid air the observed twenty-eight characteristic distances prevented interpretation. In the above experiment the hydrogen chloride was examined on a metal plate on which it had been condensed in *vacuo* by liquid air. This may have resulted in the presence of two forms simultaneously. If such was the case an experiment in which a second exposure, made after the material has been allowed to warm somewhat above the temperature of liquid air and then been recooled, would result in the disappearance of approximately one-half of the characteristic distances. By difference this would enable the identification of both forms occurring in the mixture. It would also seem that the observed intensities might assist in the interpretation of the data as they are, unless chance provided two forms in nearly equal proportion. Simon and Simson did not include the data.

Pink hydrogen chloride has also been observed by Loeb[4] to whom we had suggested our technique of preparation.

Purity of Hydrogen Chloride.—As previously mentioned, hydrogen chloride prepared from sodium chloride and sulfuric acid and further dried with sulfuric acid and phosphorus pentoxide contained considerable

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[3] Simon and Simson, *Z. Physik*, 21, 168 (1924).

[4] Loeb, *Proc. Nat. Acad. Sci.*, 12, 35 (1926).

impurity. It was noticed that the amount of impurity increased when the amount of phosphorus pentoxide used for drying was increased. After evaporation-of the hydrogen chloride, there remained a white solid which melted near the ice point, and a test on a water solution of the material showed the presence of phosphate. It seems probable that the material was phosphorus oxychloride, $POCl_3$, which melts at 1.25° and may be prepared by the interaction of hot hydrogen chloride and phosphorus pentoxide.

The method finally adopted for drying made use of concentrated sulfuric acid followed by liquefaction in a bulb containing phosphorus pentoxide and maintained at a temperature of approximately 195°K. by solid carbon dioxide and ether for about a week. The liquid hydrogen chloride was intimately mixed with a large amont of phosphorus pentoxide. The liquid was then repeatedly fractionated, the middle fractions being retained.

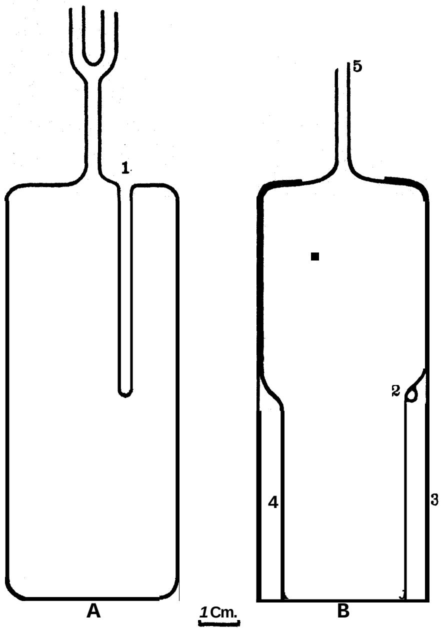

Fig. 1.

Apparatus for Vapor Pressures and for First Heats of Vaporization.—The apparatus used for temperature control was the same one used for calorimetric purposes by Gibson and Giauque,[5] except that the copper calorimeter was replaced by one of glass. Several glass containers were tried, none of which were very satisfactory since they often cracked when the hydrogen chloride was cooled to the temperature of liquid air. The first type tried is shown at A in Fig. 1. This type on two occasions broke at point 1 where the tube for holding the thermocouple was set into the container. Two glass tubes of about 2.5 mm. inside diameter are shown attached to container A. One of these was attached to a manometer while the other served as an inlet and outlet tube. When heat was introduced for the purpose of measuring the heat of vaporization it was found by means of the separate tube to the manometer that the pressure increase inside the calorimeter was less than 1 mm. of Hg and thereafter the second tube was discarded. The heater covered only the lower half of the glass vessel since it was desirable not to supply heat to the material which had been evaporated. For this reason only the material in the upper half of the calorimeter was used for heat of vaporization measurements.

The final glass calorimeter used is shown at B in Fig. 1. The thermocouple was placed in a long glass pocket shown at 2. The pocket was filled with paraffin to improve thermal contact. A copper sheath shown at 3 was shrunk on to the upper portion of B. This acted as a radiation shield for the number thirty constantan wire heater, shown at 4, returning radiated heat to the calorimeter. A thermocouple was also attached to

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[5] Gibson and Giauque, THIS JOURNAL, 45, 93 (1923).

the sheath. To assist heat conduction a heavy sheet of platinum was coiled and placed in the interior of the glass calorimeter. Platinum was used because the better conducting gold was not immediately available. The inlet tube was closely wound with a heater of number thirty constantan wire which could be used to avoid the presence of solid within the tube. The inlet tube was sealed to the protective copper cylinder by Rose metal at point 5, Fig. 1. The vapor pressures were measured by means of a manometer constructed of Pyrex glass tubing 2 cm. in diameter, and a Société Génévoise cathetometer accurate to a few hundredths of a millimeter and with a precision of 0.01 mm. A trap filled with thin gold foil protected the calorimeter against distillation of mercury from the manometer. The copper-constantan thermocouple used for the vapor pressure measurements was calibrated by means of the transition, melting and boiling point temperatures of hydrogen chloride. Our determination of these temperatures on the absolute scale will be described later in this paper.

Vapor Pressure Results.—The vapor pressures of solid hydrogen chloride are given in Table I. The pressures are expressed in international cm. of Hg. The calculated pressures given in the third column were obtained from the equation.

$$\log P(\text{cm. Hg}) = -\frac{1114}{T} - 1.285 \log T - 0.0009467T + 11.00500 \quad (1)$$

The constants of equation (1) were chosen to fit the observed data.

TABLE I

VAPOR PRESSURES OF SOLID HYDROGEN CHLORIDE

T, °K.	$P_{\text{obs.}}$, international cm. of Hg	$P_{\text{calcd.}}$	$T_{\text{obs.}} - T_{\text{calcd.}}$
132.48	0.558	0.554	−0.05
132.82	.589	.580	− .12
135.20	.787	.797	+ .10
139.23	1.308	1.310	+ .01
143.00	2.044	2.041	− .01
145.77	2.782	2.783	.00
148.44	3.705	3.709	+ .01
154.29	6.692	6.710	+ .03
155.04	7.221	7.215	− .01
158.91	10.370 10.371	10.371	.00

The vapor pressure of solid hydrogen chloride has been measured by Henglein[6] who gives the equation

$$\log P_{(\text{mm. Hg})} = -\frac{1966.3}{T^{1.1600}} + 7.5030 \quad (2)$$

and by Karwat[2] who gives an equation which is evidently in error since it does not reproduce his table of calculated data.

Henning and Stock[7] made one pressure measurement on the solid, namely, 7.56 cm. at 155.55°K. Equation (1), representing our data, gives 155.57°K. for the temperature corresponding to that pressure.

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[6] Henglein, Z. Physik, 18, 64 (1923).

[7] Henning and Stock, Z. Physik, 4, 226 (1921).

Near the melting point Equation (1) gives values 0.16' lower than that of Henglein (2) and 0.44' lower than the calculated value of Karwat. In the region about 130°K. Equation (1) gives values 0.35' higher than that of Henglein (2) and 0.36' lower than the calculated value of Karwat. Henglein evidently failed to observe the melting point since he records a pressure of 12.22 cm. for the solid at 161.0°K.; whereas our measurements show a pressure of 10.371 cm. at the triple point, 158.91°K. In addition to our triple point pressure data recorded in Table I, two preliminary measurements, made about a year previous with a less precise cathetometer, had each given 10.370 ± 0.005 cm. Karwat's observed value was 10.344 cm. at 159.34°K.

The vapor pressure data on liquid hydrogen chloride are given in Table II. The calculated pressures given in the third column are obtained from the equation of Henning and Stock[7]

$$\log P_{(\text{mm. Hg})} = -\frac{905.53}{T} + 1.75 \log T - 0.005077T + 4.65739 \qquad (3)$$

The observed differences tabulated in Col. 4 show very close agreement of our data with those of Henning and Stock. Our temperatures may be in error by 0.05' in an absolute sense while having a higher relative accuracy.

The vapor pressure of liquid hydrogen chloride has also been measured by **McIntosh** and Steele.[8] However, their temperatures appear to be 0.3" too high near the melting point and about 2.0' too high at the boiling point.

TABLE II

VAPOR PRESSURES OF LIQUID HYDROGEN CHLORIDE

T, °K.	$P_{\text{obs.}}$, international cm. of Hg	$P_{\text{calcd.}}$	$T_{\text{obs.}} - T_{\text{calcd.}}$
158.91	10.371	10.357	−0.02
164.62	16.29	16.26	− .03
169.28	22.98	22.93	− .03
173.95	31.71	31.72	.00
178.53	42.81	42.83	+ .01
181.84	52.64	52.65	.00
185.17	64.34	64.29	− .01
188.41	77.48	77.47	.00
191.96	94.39	94.28	− .02
195.93	116.51	116.33	− .03

Calorimetric Apparatus.—The copper sheathed glass apparatus used for the vapor pressure measurements could have been used for heat capacity measurements. However, it was known from the experience of others in this Laboratory that glass calorimeters were unsatisfactory, principally because the poor thermal conductivity decreases the accuracy with which small temperature intervals can be measured. For this

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[8] McIntosh and Steele, *Z. physik. Chem.*, 55, 129 (1906).

reason no heat capacity measurements were made with the **glass** apparatus, although measurements of the heat of vaporization were made by a method which avoided the necessity of high precision in the measurement of temperature. This will be discussed later in this paper. The major purpose of the glass calorimeter had been for the acquisition of experience before proceeding to the construction of a more elaborate apparatus.

For purposes of identification we shall in future papers refer to the calorimeter described below as gold calorimeter II. This calorimeter is shown in Fig. 2. The cylindrical calorimeter **A** was made from gold sheet 0.75 mm. in thickness, with welded seams. The height was **12** cm. and the diameter 3.75 cm. Twelve radial vanes were placed inside to assist in attaining temperature equilibrium. The gases were introduced through a glass tube, of inside diameter about 2.5 mm., which was sealed to a short platinum tube, extending from the top of the calorimeter, by means of a lead and a cobalt-lead glass seal. The glass inlet tube was wound with a heater similar to that used in the glass calorimeter. **A** combined resistance thermometer-heater[9] was used for measuring temperature intervals and introducing energy. This was made of gold since it was to be wound on the gold calorimeter, thus minimizing strain due to temperature change. **A** gold thermometer had previously been used by Keesom and Onnes.[10] The gold from which the thermometer wire was made contained 0.175% of silver, which was desirable, since Onnes and Clay[11] have found that the presence of silver prevents the resistance from falling to small values at low temperatures. This was advantageous since the wire was also used for heating. The gold was drawn to a diameter of 0.025 cm. (B. and S. No. 30) through steel dies, being washed with nitric and sulfuric acids after every pull, as recommended by Onnes and Clay.[11] Diamond dies were then used to reduce the diameter to 0.008 cm. (B. and S. No. 40). The wire was annealed after the last pull and then doubly insulated with silk. The construction of the thermometer-heater was as follows. The sides of the gold calorimeter were coated with Bakelite lacquer and baked at 110° for thirty minutes. The wire was then wound on, impregnated with Bakelite lacquer and dried for one week. The exterior was then coated with gold leaf to minimize radiation. Following this the calorimeter was heated to 120° for a few minutes.

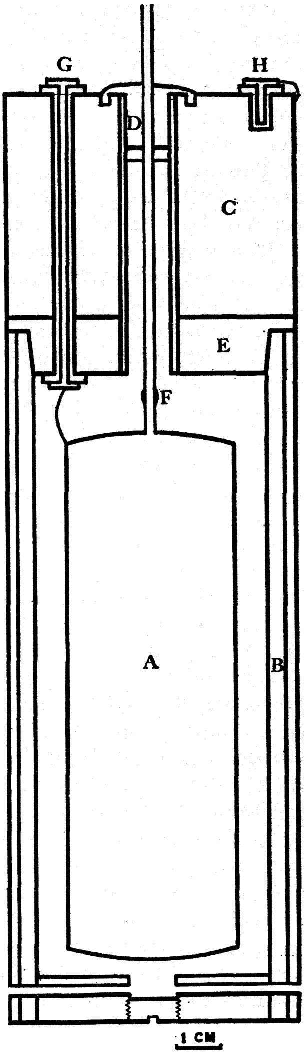

Fig. 2.

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[9] Eucken, *Physik. Z.*, 10, 586 (1909).

[10] Keesom and Onnes, *Comm.* Phys. Lab. *Univ. Leiden*, No. 143 **(1914).**

[11] Onnes and Clay, *ibid.*, No. 99c (1907).

The thermometer-heater was divided into two approximately equal parts. The total was used in all measurements except for the determinations of the heat of vaporization, in which case the lower half was used for energy input. The total resistance at room temperature was about 350 ohms and decreased to about 81 ohms at 15° K. From the results of Onnes and Clay we had expected the resistance to be less than 30 ohms at 15° K. At each end and in the center of the thermometer a lead wire of size B. and S. No. 30 copper was attached and brought into good thermal contact with the calorimeter to prevent possible gold-copper thermo-electric effects. This wire was connected to the thermometer terminals by means of 2.5 cm. of B. and S. No. 40 copper wire. One of the thermometer terminals is shown at G, Fig. 2.

The calorimeter was suspended by means of the glass connecting tube which was fastened to the protective cylinder C by means of Rose metal, shown at D, Fig. 2. The Rose metal also greatly diminished heat leak along the glass tube from above.

The protective cylinder consisted of 1750 g. of lead located in the upper portion, while the exterior walls and the lower portion of the cylinder consisted of 1850 g. of copper. The other details, such as the electrical connections and heaters for the protective cylinder, the vacuum-tight joint in the steel container for the apparatus, the high vacuum system, apparatus and methods for the electrical measurements necessary for the determination of energy and temperature were essentially the same as those described by Gibson and Giauque.[5]

The temperature of the protective cylinder and that of the steel container were obtained by means of thermocouples. The protective cylinder was suspended from the cover of the steel container by means of heavy string.

A hydrogen liquefier was located directly above the steel container. The interchanger was made from 160 meters of copper tubing of 0.2 cm. inside diameter and walls 0.05 cm. thick. The steel container and the interchanger were enclosed in a large Pyrex glass Dewar tube of about 11 cm. inside diameter and 74 cm. inside depth. The expansion valve of the liquefier could be controlled by a valve stem leading out of the apparatus. An insulated tube was included by which warm hydrogen could be blown on the valve in case of stoppage by solidified air which might accidentally get inside the hydrogen cycle. By this device the valve could be warmed sufficiently within a minute and without warming the interchanger to any great extent. Proper care in keeping the hydrogen pure made it unnecessary to make much use of the valve warmer, but it has proved valuable on several occasions. The large Dewar tube was enclosed in a vacuum-tight Monel Metal container which could be immersed in liquid air, although this was ordinarily unnecessary even when hydrogen was being liquefied. Directly above the cover of the Monel Metal container was a precooling coil consisting of about 15 meters of copper tubing similar to that in the interchanger. The precooling coil could be immersed in liquid air which, after evaporation, was utilized to surround the exterior of the whole apparatus with cold air, thus making unnecessary the immersion referred to above. In addition to the interchanger and precooler already referred to, there was a pre-interchanger to interchange heat between the temperature of liquid air and that of the room. This pre-interchanger consisted of 40 meters of copper tubing in each of four parallel tubes to eliminate a large pressure drop. The general plan of the liquefier and hydrogen cycle was similar to that described by Latimer, Buffington and Hoenshel.[12]

The hydrogen compressor delivered about 0.45 cubic meter (16 cubic feet) of hydrogen per minute at 160 atmospheres. A cast iron gas meter of large capacity in the hydrogen return line was very valuable for control purposes. A vacuum pump with a displacement of 4.25 cubic meters (150 cu. ft.) per minute was used to reduce

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[12] Latimer, Buffington and Hoenshel, THIS JOURNAL, 47, 1571 (1925).

the temperature of the liquid air or liquid hydrogen by evaporation at low pressures. This pump would reduce the pressure to 2.5 cm. of mercury.

Calibration of Resistance Thermometer.—The resistance thermometer was calibrated by means of standard copper-constantan thermocouple No. 18 which had been calibrated in terms of a hydrogen gas thermometer by Giauque, Buffington and Schulze[13] and a hydrogen vapor pressure thermometer by Giauque, Johnston and Kelley.[14] The thermocouple was used under as nearly as possible the same conditions as those existing in the original calibration. Since it was very important to carry out the calibration while the measurements were in progress, this was our invariable procedure. The high precision of the resistance thermometer enabled the measurement of small temperature intervals with an accuracy unattainable with the thermocouple alone. The absolute temperatures given are believed to be accurate to 0.05°. The resistance thermometer calibration data were treated by a graphical method which consisted of plotting deviations from a linear equation, except at the temperatures of liquid hydrogen where a large plot of resistance against temperature proved to be more convenient.

Measurement of Heat Capacities.—The method of calculating energy input, heat transfer from the surroundings and temperature rise was similar to that used by Gibson and Giauque.5 However, we have investigated more thoroughly a small source of error in the measurement of an increment of temperature. The necessity for a correction to the temperature rise observed on the resistance thermometer arises in the following manner. Excepting the lowest temperatures of measurement, the protective cylinder was maintained at a temperature slightly above the final temperature attained in a heat capacity determination. This was in order to avoid distillation from the calorimeter into that portion of the inlet tube in thermal contact with the protective cylinder. Thus at all times the calorimeter was receiving a small amount of heat from its surroundings. It is obvious that any sort of thermometer located on the exterior of the calorimeter would record a temperature above that of the average temperature since the distribution of heat requires a thermal head. Favorable location of a thermometer in the interior of a calorimeter might reduce this effect, but would make it nearly impossible to apply a correction. The necessary data for making the correction were supplied by the measurements of current and voltage during energy input. From these data the resistance and therefore the temperature of the thermometer-heater wire at any time during energy input could be calculated. The average temperature of the calorimeter at the corresponding time was known. The rate of energy input being known, it was possible to

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[13] Giauque, Buffington and Schulze, THIS JOURNAL, 49, **2343** (1927).

[14] Giauque, Johnston and Kelley, *ibid.*, 49, **2367** (1927).

determine the relation of thermal head to energy flow. This permitted the estimation of the thermal head due to an observed heat leak. In gold calorimeter II this correction was usually about one-tenth of one per cent, or less, and did not exceed three-tenths of one per cent. When this correction is not made the heat capacity results will be high. This is general for any temperature relation of calorimeter and its surroundings, provided the temperature of the surroundings is constant during a measurement. A calorimeter with poor heat conductivity will have a relatively large correction of this sort. This is particularly true when such a calorimeter is made of glass. The thermal head between the thermometer-heater wire and the average location of heat capacity in gold calorimeter II was ordinarily about one degree or less during energy input. This temporary rise in the external temperature of the calorimeter was considered in correcting for the heat received from the surroundings.

During the heat capacity measurements a small amount of material evaporated into the unfilled volume of the calorimeter and into the line. It was necessary to record the pressure at the beginning and end of each heat capacity determination in order to correct for the heat absorption accompanying this effect.

The density of solid hydrogen chloride has been determined by Simon and Simson,[3] while that of liquid hydrogen chloride has been determined by Baumé and Perrot.[15]

Heat Capacity Data.—The heat capacity data of hydrogen chloride are given in Table III. The first column contains the absolute temperature and the second column the heat capacity in calories per mole per degree.

TABLE III

HEAT CAPACITY OF HYDROGEN CHLORIDE

Molecular weight, 36.456

T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.	T, °K.	C_p/mole in cal./deg.
17.29	1.031	67.85	5.848	117.30	10.14
21.34	1.637	72.63	6.159	123.92	10.46
24.71	2.066	75.46	6.329	131.18	10.67
26.85	2.330	77.65	6.526	138.79	10.95
28.10	2.491	80.25	6.712	148.90	11.34
31.89	2.943	82.63	6.894	155.06	11.65
35.82	3.393	84.69	7.053	158.91	Melting point
39.95	3.794	87.70	7.327	163.72	13.89
44.20	4.132	88.79	7.410	171.45	13.95
48.62	4.472	92.83	7.786	171.74	13.95
51.23	4.877	92.96	7.849	178.64	14.01
56.01	5.070	98.36	Transition	185.20	14.07
58.94	5.231	103.01	9.64	188.07	Boiling point
63.31	6.650				

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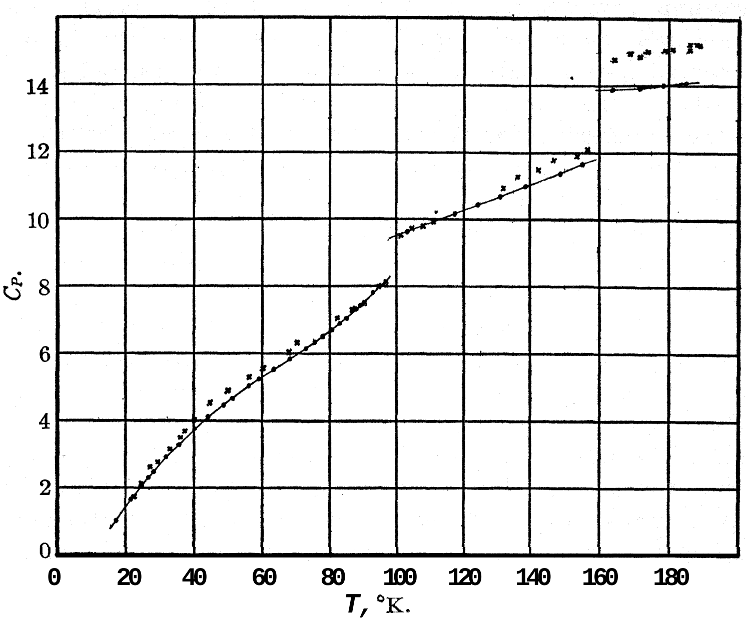
[15] Baumé and Perrot, J. chim. phys., 12, 225 (1914).

The above results are shown graphically by means of the points with the connecting curve in Fig. 3. The results of Eucken and Karwat are plotted as crosses. The measurements are in agreement at the temperatures of liquid hydrogen and of liquid air, but at all other temperatures the values of Eucken and Karwat are higher. It is difficult to explain such large discrepancies as those indicated. It appears that the temperature scale of Eucken and Karwat was somewhat in error, since they record the transition temperature as 98.75°K. as compared with our 98.36 ± 0.05°K., while Karwat gives the melting point as 159.34°K. as compared with our 158.91 ± 0.05°K. However, since the results deviate in only one direction it is improbable that the difficulty can be primarily due to an inaccurate temperature scale. Even an approximate knowledge of the extremes of the temperature range investigated would mean that if some results were too high others would necessarily be made too low. It does not seem possible to attribute the unsystematic deviations to incorrect standards of e.m.f. or resistance necessary for the energy measurements. Our standards were either calibrated by the U. S. Bureau of Standards or compared with standards newly received from the Bureau both before and after the experiments. Our standard of time was obtained from the astronomical observatory of this University. We believe that the error in the results of Eucken and Karwat is due primarily to the



X Eucken and Karwat. ● Giauque and Wiebe.

Fig. 3.—Heat capacity in calories per mole of hydrogen chloride.

use of too small an amount of material, and secondarily due to the use of a poorly conducting glass calorimeter. The amount of hydrogen chloride used by Eucken and Karwat was about **0.17** mole, whereas **3.72** and **3.57** moles were used in our experiments.

Nearly all of our measurements fall within 0.1 or **0.2%** of a smooth curve through the points. A few are off by about 0.5%. A smooth curve through the data should represent the heat capacity to an accuracy of about 0.2%, except in the case of the lowest measurement where, as the result of a poor vacuum and other experimental difficulties, the value may be in error by over 1%.

Transition Temperature and Melting Point Temperature.—Both the transition and the melting point temperatures were very sharp. Each was observed over a period of several days with occasional small input of energy and return of equilibrium. The temperature of the protective cylinder was maintained very closely at the same temperature as the calorimeter during these measurements. At the transition temperature the resistance thermometer showed an extreme variation of 0.02° over a period of seventy hours, while during the same time interval the thermocouple varied over a range of 0.05°. The transition temperature was **98.36** ± 0.05°K.

At the melting point an extreme variation of 0.01° was observed on the resistance thermometer over a period of seventy hours, while the thermocouple varied over a range of **0.06"**. The melting point temperature was **158.91** ± 0.05°K.

Heats of Fusion **and** of Transition.—The heat of fusion and that of transition were measured in the usual way of starting the heat input at a temperature somewhat below the melting or transition temperature and ending the input when the temperature had risen somewhat above. A correction for the $\int CpdT$ was applied. The results are given in Table

TABLE IV

HEAT OF TRANSITION OF HYDROGEN CHLORIDE

ΔH in Calories per Mole

Temp., °K.	G. and W.	Average	E. and K.	Average
98.36	284.2	284.3	290.0	293.8
	284.2		291.7	
	284.5		293.2	
			299.2	

HEAT OF FUSION OF HYDROGEN CHLORIDE

Temp., °K.	G. and W.	Average	E. and K.	Average
158.91	476.5	476.0	504.5	504.5
	475.6		506.5	
			505.5	
			504.5	
			502.5	

IV in the column headed G. and W. The results of Eucken and Karwat[1] are included for comparison.

Karwat[2] has calculated the heat of fusion from his measurements of the vapor pressure of solid hydrogen chloride combined with those of Henning and Stock on the liquid. He obtains the value 498.2 cal. per mole, in fair agreement with the calorimetric value of 504.5 obtained by Eucken and Karwat. A similar calculation based on our vapor pressure data leads to a value of 462 cal. per mole. However, we can expect no high accuracy from this calculation and we give it no weight as compared with our calorimetric value of 476.0. In the above calculation the equation of Berthelot was assumed in correcting for the imperfection in the gas state. The above correction lowered the value only by about three calories below the value which would have been obtained on the assumption of a perfect gas.

Measurement of **the** Heat of Vaporization.—The amount of material evaporated was obtained by absorption in a solution of 30% sodium hydroxide. The gas was bubbled through a small mercury trap in the bottom of the absorption bulb. The absorption solution was protected by two U-tubes, each containing on one side calcium chloride and on the other soda lime. One of the U-tubes was removable for weighing.

Two methods of measurement were employed. The first one designated as I in the tables was as follows. Two identical absorption bulbs were attached to a line leading from the calorimeter in such a way that a three-way stopcock controlled the flow of gas. The heating current was turned on and the stopcock opened into one of the absorption bulbs. After several minutes a steady state was reached and the stopcock was turned to direct the flow of gas into the other bulb. At the same time a calibrated stopwatch was started. The pressure remained constant to one millimeter. The second method, designated II in the tables, was as follows. With one absorption bulb on the line and the stopcock closed, the warming rate was observed as in a heat capacity determination. Then at a predetermined time the current was turned on, the stopwatch started, and shortly after this the stopcock was opened. At the end the current was turned off and after the flow of gas had practically ceased the stopcock was closed and the warming rate again taken. In both methods a correction for heat received from the surroundings during a run was made on the assumption of Newton's law of heat transfer and our knowledge of the temperature of the exterior of the calorimeter. In gold calorimeter II the external temperature was obtained as an average of the wall, by means of the thermometer-heater, of the bottom, by means of the attached thermocouple, and of the top, from the evaporation temperature as indicated by the pressure. The external temperature was about one degree above the evaporation temperature. The temperature of the protective cylinder and that of the steel container were kept above the evaporation temperature to prevent condensation. The container temperature was controlled by means of solid carbon dioxide condensed on its surface. The temperature of the solid carbon dioxide was controlled by reduced pressure. The hydrogen chloride was evaporated in amounts of from 10 to 15 g. for each determination. Only the liquid above the heater was used for this purpose. The determinations made with gold calorimeter II utilized the material on which the measurements of heat capacity had been made. The initial and final pressures were observed for each determination and a small correction was made for the amount of material in the line volume which was known by calibration. From the known density of liquid hydrogen chloride the correction for the volume of the liquid replaced by gas could be made. Method II involved a knowledge of the heat capacity of calorimeter and substance.

We feel more confidence in Method II, and the results obtained by this method show a smaller deviation from the mean than do those obtained by Method I. The results on the heat of vaporization at one atmosphere are given in Table V. The actual evaporation pressures were slightly above one atmosphere, but a small correction has been made to allow for this. Method I was used only with the glass calorimeter which was somewhat of a handicap, although the copper sheath and the coiled platinum sheet in the interior removed most of the disadvantages of the glass type of apparatus. The agreement, to one calorie, of the average values obtained from the two different methods and calorimeters must be regarded as fortuitous. In the measurements with the glass calorimeter the rate of evaporation was varied by a factor of more than three without producing any systematic deviation of the results. Also, the total amount of material within the calorimeter seemed to produce no appreciable effect. The slow evaporation rate of less than one-third mole per hour, which was used in the final measurements, eliminated the possibility of any appreciable loss due to spray. Observation on exposed glass bulbs of similar cross section, and a rate of evaporation many times that of any used, showed that evaporation proceeded without the formation of visible bubbles.

TABLE V

HEAT OF VAPORIZATION OF HYDROGEN CHLORIDE

Boiling point, 188.07° K. Molecular weight, 36.456

Moles of HC1 evaporated	Type of run	Time of energy input in min.	AH at 760 mm. Hg in cal./mole	Remarks
0.3621	I	29	3858	
.4000	I	40	3852	Pyrex glass calorimeter
.2848	I	60	3871	
.2769	I	60	3871	
.2717	I	75	3857	
.2729	I	75	3854	
.3068	I	75	3851	
Mean			3859 * 9	
0.3316	II	80	3859	
.3083	II	80	3866	Gold Calorimeter II
.3192	II	80	3851	
.4746	II	120	3861	
.4683	II	120	3862	
Mean			3860 * 4	Best value

The heat of vaporization of hydrogen chloride has been determined directly or by calculation from vapor pressure measurements by a number of observers. While the accuracy of these various results is such that they can be given no weight, we include them as Table VI for the sake of completeness.

TABLE VI

PREVIOUSLY PUBLISHED VALUES OF HEAT OF VAPORIZATION OF HYDROGEN CHLORIDE

AH. cal./mole	Method	Observer
3540	**Indirect**	**McIntosh and Steele[8] (1906)**
3560	**Direct**	**Elliott and McIntosh[16] (1908)**
3601	**Direct**	**Estreicher and Schnerr[17] (1910)**
4040	**Indirect**	**Henglein[6] (1923)**

In the two indirect determinations given above the gas was assumed to be perfect. This assumption leads to serious error in such calculations. For example, if we make use of the algebraically convenient equation of state of Berthelot

$$PV = RT\left[1 + \frac{9PT_c}{128P_cT}\left(1 - 6\frac{T_c^2}{T^2}\right)\right]$$

combined with the thermodynamic equation $\frac{dP}{dT} = \frac{AH}{TAV}$, the density of liquid hydrogen chloride as given by Baumé and Perrot,[15] namely 1.706–0.00276T, and the equation of Henning and Stock which is in agreement with our data for the vapor pressure of liquid hydrogen chloride, we obtain the value of **3881** cal. per mole. Considering the assumption, this value compares favorably with our direct determination of **3860.** However, we hasten to add that this approximate agreement should be taken to indicate that Berthelot's equation happens to represent the deviation of hydrogen chloride from the gas law rather than as a confirmation of our value for the heat of vaporization. The similar use of van der Waals' equation leads to a more inaccurate value of **3932 cal./** mole.

Eucken and Donath[18] have by an ingenious and apparently quite accurate method obtained heats of condensation to the solid form for a number of gases. They state that their data on hydrogen chloride are somewhat more inaccurate than those on other substances, due to a slight amount of reaction with the metal apparatus. They give the value **4594 ± 7** cal. per mole at 156°K. Using our various calorimetric data, and assuming that Berthelot's equation may be used with the thermodynamic equation,[19]

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

to give the deviation of the heat content of the gas from that of the ideal state, we obtain a value of **4580,** which is in satisfactory agreement with

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[16] **Elliott and McIntosh, *J. Phys. Chem.*, 12, 163 (1908).**

[17] **Estreicher and Schnerr, Bull. *intern. acad. sci. Cracovie, A, 345* (1910).**

[18] **Eucken and Donath. *Z. physik. Chem.*, 124, 181 (1926).**

[19] **Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 163.**

the value of Eucken and Donath when it is considered that our use of Berthelot's equation involved a correction amounting to 25 cal. per mole.

The Entropy of Hydrogen Chloride from the Third Law.—The entropy of hydrogen chloride was obtained in the usual manner by graphical integration of the equation $S = \int_0^T C_p \mathrm{d} \ln T$ plus the entropy changes accompanying each change of state. In extrapolating below the lowest temperature of measurement we have made use of the Debye function with an $h\gamma/k = 128$. In doing so it has been assumed that at the lower temperatures the absorption of energy is determined by but one characteristic frequency. This assumption is based on the fact that the low temperature data show a tendency to approach a value asymptotically of about six calories per degree per mole. This may be noted in Fig. 2. It is plausible that at low temperatures molecule units in the crystal may be vibrating in a manner similar to that of a monatomic solid. The data agree quite well with the Debye function up to a temperature of 40°K. While we recognize the arbitrariness of 'the above procedure, the absolute error should be small on a total extrapolated amount of 0.30 entropy units.' A summary of the entropy calculation is given in Table VII.

TABLE VII

CALCULATION OF ENTROPY OF HYDROGEN CHLORIDE

Solid stable below 98.36°K.	Cal. per deg. per mole
0 to 16°K., extrapolation	0.30
16 to 98.36°K., graphical	7.06
Transition 284.3/98.36 =	2.89
Solid stable above 98.36°K.	...
98.36 to 158.91°K. graphical	5.05
Fusion 476.0/158.91 =	3.00
Liquid	...
158.91 to 188.07°K., graphical	2.36
Vaporization, 3860/188.07 =	20.52
Entropy of hydrogen chloride gas at boiling point =	41.2 ± 0.1 E. U.

Since we are about to compare the above value of the entropy with that obtained from theories assuming a perfect gas, it will be necessary to consider the effect due to the imperfection of hydrogen chloride gas. We have previously shown that Berthelot's equation of state gives the molal volume of hydrogen chloride gas with considerable accuracy. Since reliable data of state are lacking, we can do no better than to use Berthelot's equation in the calculation of this correction. Combining this with the thermodynamic equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$ we obtain for the entropy change accompanying expansion from one atmosphere to zero pressure

$$\Delta S = -R\left[\int_{P=1}^{P=0} \mathrm{d} \ln P + \frac{27T_c^3}{32T^3P_c}\int_{P=1}^{P=0} \mathrm{d}P\right]$$

The entropy change accompanying compression from zero pressure to an ideal state of one atmosphere (fugacity = 1) is given by

$$\Delta S = -R \int_{P = 0}^{P = 1} P = 0 \; \mathrm{d} \ln P$$

Combining, it is found that the entropy of a Berthelot gas is lower than that of ideal gas by an amount of $R27T_c^3P/32T^3P_c$. For hydrogen chloride at its boiling point this amounts to 0.10 cal./deg. per mole.

Theoretical Calculation of the Entropy of Hydrogen Chloride from Spectroscopic Data.—The entropy of a gas may be considered to consist of two parts, first, that resulting from the volume and the translational motion of the molecules and, second, that resulting from all the other degrees of freedom. It is best not to separate the treatment of these latter degrees of freedom, since the absorption of energy by one often has an appreciable effect on the others.

The first portion may be obtained from the Sackur equation[20] where

$$S = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln V + S_0$$

S = entropy per mole, R = gas constant per mole, M = the molecular weight, V = the molal volume and S_0 = a constant. The form of this equation has been supported by considerable data. There are, however, two theoretical methods of evaluating S_0 which lead to nearly the same value and yet are apparently irreconcilable since each makes use of natural constants known to a considerable degree of accuracy. Neither is free from questionable assumption. The first method[20,21,22] makes use of quantum assumptions and statistical mechanics. The second method is used by Lewis[23] and is based on the theory of ultimate rational units proposed by Lewis and Adams.[24]

The expression for the constant as determined by Tetrode is

$$S_0 = R \ln \frac{(2\pi k)^{3/2}\, e^{5/2}}{h^3\, N^{5/2}} = -11.06$$

The expression obtained from U. R. U. is

$$S_0 = R \ln \frac{k^{3/2}\, C^3}{N^{5/2}(4\pi l)^6} = -11.38$$

where e is the base of natural logarithms, h is Planck's constant, c the velocity of light and l the elementary electronic charge.

The values adopted for all fundamental and derived constants used in this paper are those given in the International Critical Tables.[25]

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[20] Sackur, Ann. *Physik,* 36, *968* (1911).

[21] Tetrode, *ibid.,* 38, 434 (1912).

[22] Ehrenfest and Trkal, *Proc. Akad. Sci. Amsterdam, 23,* 162 (1920).

[23] Lewis, *Phys. Rev.,* [2] 18, 121 (1921).

[24] Lewis and Adams, *ibid.,* [2] 3, 92 (1914).

[25] International Critical Tables, Vol. I, p. 16.

The second portion of the entropy is obtained from the spectroscopically determined possible energy states combined with some assumption as to the distribution of the molecules between these various possible states. The first calculation of this kind utilizing the actual energy levels is due to Hicks and Mitchell.[26] Their calculation is based on a choice of a *priori* probabilities, 2, 4, 6, etc., which now appear to be incorrect. Also, they neglected to include the zero point entropy of R ln 2 which results from a weight of 2 for the initial state. Hicks and Mitchell unnecessarily used a laborious method in calculating the entropy. This was due to their failure to observe that theoretical equations of the type concerned can be integrated exactly even when the actual quantum states are used. Since they had calculated values of the heat capacity at various temperatures, they obtained that fraction of the entropy concerned by graphical integration of $S = \int_0^T C\, d \ln T$. It will be shown in the following paragraphs that the calculation of entropy from spectroscopic data involves less expenditure of labor than is necessary to obtain the heat capacity at **a** single temperature and, moreover, involves the use of summations which are common to both calculations. The value of this observation will be more apparent to those who undertake the labor required for calculations of this type.

In addition to translational energy, hydrogen chloride has, at ordinary temperatures, nearly fully excited rotational energy and a small amount of vibration. The integration required in the calculation of the rotational entropy of a rigid molecule has been performed by Urey[27] graphically, and by Tolman and Badger,[28] who substituted the limitation of rigidity before carrying out the integration. Hicks and Mitchell have tabulated the total energy above the zero point state for a sufficient number of the rotation levels accompanying zero, one and two units of vibration. Following the usual nomenclature, we designate, by Em,n, the energy corresponding to the state having m and n as its rotational and vibrational quantum numbers, respectively The rotational-vibrational heat capacity is then shown by Hicks and Mitchell to be

$$C_{R+V} = \frac{N}{kT^2}\left[\frac{\Sigma m\Sigma n\ pm,n\ E^2m,n\ e^{-\frac{Em,n}{kT}}}{\Sigma m\Sigma n\ pm,n\ e^{-\frac{Em,n}{kT}}} - \left(\frac{\Sigma m\Sigma n\ pm,n\ Em,n\ e^{-\frac{Em,n}{kT}}}{\Sigma m\Sigma n\ pm,n\ e^{-\frac{Em,n}{kT}}}\right)^2\right]$$

where pm,n is the a *priori* probability, k is Boltzmann's constant, and N is Avogadro's number. As is well known, an expression of this type may be written as

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[26] **Hicks** and Mitchell, THIS JOURNAL, 48, **1520 (1926).**

[27] **Urey,** *ibid.*, 45, **1445 (1923).**

[28] **Tolman and Badger,** *ibid.*, 45, **2277 (1923).**

$$C_{R+V} = \frac{R}{T^2}\frac{\mathrm{d}^2 \ln Q}{\mathrm{d}\left(\frac{1}{T}\right)^2}$$

where Q represents the distribution function $\Sigma m \Sigma n \; p_{m,n} \; e^{-\frac{E_{m,n}}{kT}}$; for example, see Reiche.[29] Then using the same integral as that used by Tolman and Badger

$$S_{R+V} = \int_0^T \frac{R}{T^2}\frac{\mathrm{d}^2 \ln Q}{\mathrm{d}\left(\frac{1}{T}\right)^2}\,\mathrm{d}\ln T$$

$$= R\left[\ln Q - \frac{1}{T}\frac{\mathrm{d}\ln Q}{\mathrm{d}\left(\frac{1}{T}\right)}\right]_0^T$$

$$= R\left[\ln \Sigma m \Sigma n \; p_{m,n} \; e^{-\frac{E_{m,n}}{kT}} + \frac{1}{kT}\cdot\frac{\Sigma m \Sigma n \; p_{m,n} \; E_{m,n} \; e^{-\frac{E_{m,n}}{kT}}}{\Sigma m \Sigma n \; p_{m,n} \; e^{-\frac{E_{m,n}}{kT}}}\right]_0^T$$

It may be observed that the only assumption concerning $p_{m,n}$ and $E_{m,n}$ is that they are independent of temperature. The above method also holds if an electronic transition is included in the energy absorption. In summing the above series we have used the *a priori* probabilities 1, 3, 5, 7, etc., corresponding to the respective quantum states $^1/_2$, $^3/_2$, $^5/_2$, $^7/_2$, etc. Each vibrational state has been given unit weight; thus $p_{m,n}$ is essentially p_m. The use of $p_m = 2m$ is supported by the intensity measurements of Bourgin[30] on the absorption spectrum of hydrogen chloride He shows that his data correspond with the above weights in agreement with the requirements of the wave mechanics theory of Schrodinger.

Kemble[31] has carried out a re-analysis of the data of Colby, Meyer and Bronk[32] on the infra-red absorption bands of hydrogen chloride. He presents the results in the form of equations with estimates of the probable error of the coefficients. From these equations, which apply to the lighter isotope, may be obtained the energies of the various states with which we are concerned. We have used these more accurate values in preference to the data as tabulated by Hicks and Mitchell. It is particularly important to have accurate values for the energies of the first few states.

A consideration of the isotope effect on the rotational-vibrational entropy shows that the use of the data for the lighter isotope leads to a value which is low by only 0.0016 cal./deg. per mole.

With the above data and method we have calculated the value of the entropy of ideal hydrogen chloride at the temperature of its boiling point,

[29] Reiche, *Ann. Physik.* 58, 657 (1919).

[30] Bourgin, *Phys. Rev.*, 29, 794 (1927).

[31] Kemble, *J. Optical Soc. Am.*, 12, 1 (1926).

[32] Colby, Meyer and Bronk, *Astrophys. J.*, 57, 7 (1923).

188.07°K. The value obtained is 41.45 or 41.13 cal./deg. per mole corresponding, respectively, to the use of the Tetrode or Lewis constant for the Sackur equation. A similar calculation has been made for a temperature of 298.1°K. (25°C.). These results are compared with the experimental values in Table VIII. We believe that our experimental value for the actual gas at 188.07°K. is accurate to about 0.1 cal./deg. per mole. This is based on the assumption of no appreciable error in the 0.3 entropy units extrapolated. We hesitate to estimate the accuracy with which Berthelot's equation gives the correction from the actual to the ideal state Fortunately this correction is small. The necessity for this correction may be eliminated by obtaining the entropy of the gas through use of the vapor pressure and entropy of the solid. At these lower pressures the error introduced by the use of such an equation as that of Berthelot is negligible. Such a calculation, making use of vapor pressure equation (1) at the melting point temperature, 158.91°K., leads to a value of 41.2 E. U. for the entropy of ideal hydrogen chloride at 188.07°K. A similar calculation starting at 132°K. leads to a value of 41.3 E. U.

While this method eliminates an uncertain correction, we believe our first method to be more reliable. Fortunately both methods lead to the same value. The "experimental" value given for 298.1°K. was obtained by adding the theoretical difference between 188.07°K. and 298.1°K. to the 41.3 cal./deg. per mole obtained at 188.07°K.

TABLE VIII

COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES OF THE ENTROPY OF HYDROGEN CHLORIDE

	Theoretical		Experimental	
T, °K.	Tetrode constant	Lewis constant	Actual gas	Corrected to ideal state
188.07	41.45	41.13	41.2 ± 0.1	41.3
298.1	44.64	44.32	......	44.5

Eucken, Karwat and Fried[33] have summarized the available data on condensed gases in terms of chemical constants. They have been recalculated in the form of absolute entropies in a chapter added, by the translator, to the German edition of "Thermodynamics" by Lewis and Randall.[34] The value given for the work of Eucken and Karwat[1] on hydrogen chloride is 45.4 E. U. at 298.1°K., for which these authors had expressed an accuracy of ±0.2 E. U., which definitely placed it in disagreement with the theoretical values.

The close agreement of our experimental and theoretical values is very good evidence, not only for the validity of the theoretical considera-

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[33] Eucken, Karwat and Fried, *Z. Physik*, 29, 1 (1924).

[34] "Thermodynamik und die freie Energie chemischer Substanzen," von Lewis und Randall, übersetzt von Redlich, Julius Springer, Wien, 1927.

tions as closely approximating the actual properties of the substance, but also for the third law of thermodynamics.

Tests of the Third Law.—We shall test the third law, first by means of the reactions

$$\begin{array}{llcll}
\text{(a)} & \tfrac{1}{2}\mathrm{H_2} + \tfrac{1}{2}\mathrm{Cl_2} & = & \mathrm{HCl\,(aq)}; & \Delta F^{\circ}_{298} = -31{,}375 \\
\text{(b)} & \mathrm{HCl\,(aq)} & = & \mathrm{HCl\,(g)}; & \Delta F^{\circ}_{298} = 8{,}604 \\
\hline
\text{(c)} & \tfrac{1}{2}\mathrm{H_2} + \tfrac{1}{2}\mathrm{Cl_2} & = & \mathrm{HCl\,(g)}; & \Delta F^{\circ}_{298} = -22{,}771^{35}
\end{array}$$

The free energy change of (b) is taken from the manuscript soon to be published by Randall and Young, who have reconsidered the available data, while that of (a) is taken from Lewis and Randall[36] and corrected by use of the data given by Randall and Young. The heat of reaction, ΔH, for (c) is given as 22,000 cal. by both Thomsen and Berthelot. From the relation $\Delta F = \Delta H - T\Delta S$ we find $\Delta S_{298} = 2.6$ E. U. for reaction (c). The entropy of one-half a mole of chlorine gas as given by Gerke[37] is $\frac{1}{2}S_{\mathrm{Cl_2}} = 27.1$ E. U. Bakhuyzen[38] gives a value for $\frac{1}{2}S_{\mathrm{H_2}}$ at low temperatures which leads to 14.8 E. U. at 298°K. From these data $S_{\mathrm{HCl}} = 44.5$ in exact agreement with our experimental value. Such close agreement is undoubtedly fortuitous. The principal uncertainty lies in the ΔH value given by Thomsen and by Berthelot, while the other data used may be in error by an amount corresponding to several tenths of an entropy unit.

The second test makes use of the reactions

$$\begin{array}{llcll}
\text{(d)} & \tfrac{1}{2}\mathrm{H_2} + \mathrm{HgCl} & = & \mathrm{Hg} + \mathrm{HCl\,(0.1\ M)}; & \Delta F = -\ 9{,}175 \\
\text{(e)} & \mathrm{HCl\,(0.1}\ M) & = & \mathrm{HCl\,(g)}; & \Delta F = 11{,}604 \\
\hline
\text{(f)} & \tfrac{1}{2}\mathrm{H_2} + \mathrm{HgCl} & = & \mathrm{Hg} + \mathrm{HCl(g)}: & \Delta F = 2{,}429
\end{array}$$

The free energy changes of (d) and (e) are both given by Randall and Young. Their new measurements on the mercury-calomel electrode show that the older determinations are in error due to the effect of dissolved oxygen. The ΔH for (d) is given as —8291 by Lewis[39] who measured temperature coefficients of a cell utilizing this reaction. We have calculated the heat of reaction (e) from the measurements of Wrewsky and Sawaritzky[40] and find the value 17,660 cal. for $H_{\mathrm{HCl\,(g)}} - \overline{H}_{\mathrm{HCl\,(0.1\ \mathit{M})}}$ where $\overline{H}$ refers to the partial molal heat content of hydrogen chloride in solution. Lewis and Gibson[41] give the entropy of liquid mercury $S_{\mathrm{Hg}} = 17.8$ E.U., and that of calomel $S_{\mathrm{HgCl}} = 23.2$. Thus we find $S_{\mathrm{HCl}} = 43.5$ as against our measured value of 44.5. The difference is well within the limits

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[35] The data used for the two tests of the third law have not been corrected by use of the I. C. T. constants since the difference is not important in this case.

[36] Lewis and Randall, ref. 19, p. 502.

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

[38] Bakhuyzen, *Z. physik. Chem.,* 111, 57 (1924).

[39] Ref. 19, p. 392.

[40] Wrewsky and Sawaritzky, *Z. physik. Chem.,* 112, 90 (1924).

[41] Lewis and Gibson, THIS JOURNAL, 39, 2554 (1917).

of accuracy of the various data, the greatest uncertainty being in the heat of solution of hydrogen chloride. The older value of 17,300 found by Thomsen for this reaction would more than double the discrepancy. This again emphasizes the observation of Lewis, Gibson and Latimer[42] that as more accurate data are obtained the discrepancies from the third law are reduced,

We express our appreciation to J. A. Roebling Sons Co. for insulating the delicate gold wire, to W. J. Cummings for the glass blowing, particularly of the metal-glass seal which so successfully withstood temperature changes, and to G. F. Nelson, who was responsible for the mechanical construction of the apparatus. This assistance contributed in no small measure to the success of our experiments.

Summary

The heat capacity of the two solid forms and of liquid hydrogen chloride has been measured from 16°K. to its boiling point.

The transition temperature is 98.36 ± 0.05°K., the melting point 158.91 ± 0.05°K. and the boiling point 188.07 ± 0.05°K.

Calorimetric determinations of the heats of transition, fusion and vaporization have been made.

The vapor pressures of both solid and liquid have been measured.

What is believed to be a third crystalline form of hydrogen chloride, with a reddish pink color, has been observed.

The entropy of hydrogen chloride gas has been calculated from the calorimetric data. It has also been calculated from spectroscopic data and the Sackur equation.

The procedure for the calculation of entropy from the energy levels of a molecule as given by band spectra is discussed.

The calculated and theoretical values agree well, thus supporting not only the theoretical method but also the third law of thermodynamics.

The third law has been tested by means of two series of reactions and is further confirmed within the limits of accuracy of the data.

BERKELEY, CALIFORNIA

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[42] **Lewis, Gibson** and Latimer, THIS JOURNAL, 44, 1008 (1922).

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

THE PHOTOCHEMICAL DECOMPOSITION OF AZOMETHANE

BY HERMAN C. RAMSPERGER[1]

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The rate of the thermal decomposition of azomethane has been shown to be unimolecular over a small range of high pressures,[2,3] but the constant becomes somewhat smaller at low pressures.[4] This effect is expected if the reaction is due to molecules activated by collisions with other molecules. Rice and the author[5] considered two such theories and derived equations showing the way in which the rate would fall off with decreasing pressure. These have been applied to the decomposition of azomethane,[6] and the experimental values check one of the theories (Theory II) quite well. There is the possibility that in the case of azomethane there may be a chain reaction, especially since the reaction is certainly exothermic, as is indicated by the explosive nature of the gas.[7] This would require quite a different explanation of the reaction rate as, for example, that postulated by Christiansen and Kramers.[8]

The length of a chain reaction can be determined in the case of activation by light by measurements of the photochemical efficiency. Activation by light may produce molecules with a more definitely specified total energy and energy distribution than is the case with thermally activated molecules. This would be especially true if the light were very nearly monochromatic and if the molecule had an easily resolvable band spectrum, for then absorption of one particular spectrum line would determine both the initial and final states of the molecule. Thermally activated complex molecules would not be greatly restricted as to total energy or energy distribution. If, however, it is sufficient for reaction that a molecule have a certain minimum total energy independent of the nature of this energy, then we should expect the reaction to be similar for these photochemically activated molecules. If it is necessary that a particular degree of freedom obtain a minimum of energy, as in Theory II of Rice and Ramsperger,[5] and this energy may be obtained from any other degrees of freedom by repeated redistribution within the molecule between collisions, then it will not matter in what part of the molecule the light energy

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[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, 49, 912 (1927).

[3] Experimental work now in progress shows that the range over which the reaction is unimolecular is greater in the case of other azo compounds, as for example azo*iso*propane.

[4] Ramsperger, *ibid.*, 49, 1495 (1927).

[5] Rice and Ramsperger, *ibid.*, 49, 1617 (1927).

[6] Rice and Ramsperger (forthcoming).

[7] Thiele, *Ber.*, 42, 2575 (1909).

[8] Christiansen and Kramers, *Z. physik.* Chem., 104, 451 (1923).

was absorbed.[9] Nevertheless, the energy of a photon, or light quantum, of the light used (77,800 cal.) is so much larger than the heat of activation (51,200 cal.) that if the length of any reaction chain were a function of the energy in excess of the activation energy, the photochemical chain reaction would be even longer than the thermal one. It will be found experimentally that only about two molecules decompose for each photon absorbed. Evidence will be presented to show that the thermal decomposition also is probably not a long chain reaction.

The Absorption Curve

Liquid azomethane has a very slight yellow color. The gas would therefore be expected to have a strong absorption band in the near ultraviolet. Quantitative absorption measurements were made by the method of Ramsperger and Porter.[10]

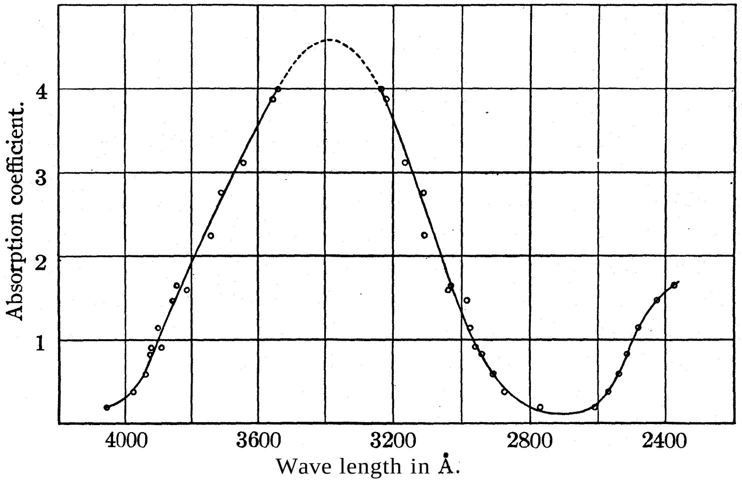

Fig. 1.—Ultraviolet absorption curve of azomethane.

Light from a quartz mercury arc was passed through a quartz cell 60 cm. long containing azomethane and was photographed with a Hilger quartz spectrograph. On the same plate another photograph was taken of the same source of light through the same cell evacuated and through a copper gauze screen of known absorption. The blackening of the plate is the same in the two photographs at any wave length for which the particular screen and the azomethane gas have the same absorption. Positions of equal intensity were determined by the method given by Ramsperger and Porter.[10] Absorption coefficients were calculated by the relation $I_t/I_0 = 10^{-ecd}$, where I_t/I_0 is the fraction of light transmitted, e is the molecular absorption coefficient, c the concentration in moles per liter and d the length of the cell (60 cm.). There was no evidence of a band spectrum. The results are given in Table I and plotted in Fig. 1.

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[9] It is possible also that the absorption of light energy will involve some energy states that do not occur at all in molecules activated thermally, and these may not have the same effect in producing reaction.

[10] Ramsperger and Porter, THIS JOURNAL, 48, 1267 (1926).

TABLE I

POINTS OF EQUAL INTENSITY (ÅNGSTRÖM UNITS)

Screen no.	Light transmitted by screen, %	Expt. 1 P = 9.01 cm. T = 20.5°	Expt. 2 P = 24.98 cm. T = 21.0°	Expt. 3 P = 5.32 cm. T = 21.0°
1	69.3	......	4060 2770 2610	3890 2960
2	48.8	......	3974 2874 2570	......
3	33.1	3815 3040	3938 2908 2538	3710 3112
4	21.2	3738 3108	3925 2942 2515	3555 3220
5	11.5	3645 3166	3900 2976 2480	......
6	6.3	3540 3236	3856 2984 2426	......
7	4.4	......	3845 3032 2374	......

Monochromatic Light

The source of light for the decomposition experiments was a vertical 220-volt Cooper-Hewitt mercury arc. An attempt was made to use a Hilger Monochromator, but the intensity of the three lines, 3663, 3654 and 3650 Å. was hardly great enough to permit accurate measurements of the decomposition. A filter was therefore used. It was a modification of the one used by Eggert and Noddack.[11] The filter cell was 5 cm. in diameter and 4.5 cm. long. A blue cobalt glass was sealed on each end of the cell in place of the ammoniacal copper sulfate solution used by Eggert and Noddack. A solution of 0.10 g. per liter of phenosaphranine was circulated through the cell at the rate of 50 cc. per hour. The transmitted light consisted almost entirely of the three lines mentioned above. This was proved by photographing the transmitted light with a quartz spectrograph. The strong blue line at 4046 Å. and several weak lines closer to the three ultraviolet lines were each about as dense as the strong line 3663 Å. was with an exposure only one-thousandth as long. No other lines were visible on the plate. However, this filter transmitted some deep red and infra-red light which had to be corrected for in the energy measurements.

Apparatus

The apparatus was arranged in the following order: the mercury arc, a quartz lens two inches in diameter and three inches in focal length, the filter cell described above, a camera shutter and then either a linear thermopile in case energy measurements were made or the quartz reaction vessel containing azomethane. The mercury arc had a metal plate attached which was as wide as the arc and 1.5 cm. high. The lens was placed so as to form a sharp image of the arc 1.85 cm. high. The thermopile was a ten-junction Coblentz linear thermopile, the slit of which was a little less in height than the image of the arc and could either be placed with the sharp image of the arc on the thermopile surfaces or could be swung through 90° to face a Bureau of Standards standard of radiation lamp exactly two meters distant. This thermopile could be moved with a screw device back and forth across the image of the arc. The quartz reaction cell was 3 cm. in diameter and 9.13 cm. long. It could be placed so that the entire beam of light came well within the cell.

Energy Measurements

A high sensitivity, low resistance, D'Arsonval galvanometer was used to measure the thermopile current. With a scale at 3.5 meters from the galvanometer large deflections were obtained. When very large deflections were to be measured a resistance of 3 ohms was shunted across the

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[11] Eggert and Noddack, *Z. Physik*, 20, 299 (1924).

galvanometer. This reduced the deflections by an experimentally determined factor of 2.61.

The general method of determining the radiation density was to move the thermopile across the image of the arc, taking readings at every millimeter near the center of the image where the radiation density was very great and every 2 mm. on the edges of the image. These deflections (properly corrected for infra-red radiation) were plotted on coordinate paper as ordinate and the position of the thermopile as abscissa. The area under this curve was determined. This area multiplied by the radiation density per sq. mm. per sec. per cm. deflection, as determined by calibration of the thermopile galvanometer arrangement against the standard lamp and then multiplied by the height of the image in mm., gives the total radiation of the three mercury lines falling per second on the cell.

The actual procedure was as follows. Before each experiment the arc was allowed to become constant, which required at least thirty minutes after starting. The thermopile was evacuated and the mercury diffusion pump was kept running during the entire experiment, as it was noticed that the thermopile sensitivity was more constant if pumping was continuous. The thermopile-galvanometer arrangement was calibrated by means of the radiation standard supplied by the Bureau of Standards and according to the specifications supplied with it. Usually about five readings were made which were constant to about 1%. The calibration was repeated after the energy measurements were complete and an average was taken. The deviation from the average was usually about 1%.

Readings were started on one edge of the image of the arc. Three readings were made at each position of the thermopile, (1) with the shutter closed; (2) with the shutter open and a sheet of "Crookes A" glass and a sheet of fused quartz in the path of the light; (3) with the shutter open and only the sheet of quartz in the path. The quartz sheet was similar to the front window of the reaction cell and the radiation passing through this sheet would correspond to the radiation entering the cell. The "Crookes A" glass absorbs all of the ultraviolet radiation, as was proved by photographing the ultraviolet spectrum with a sheet of "Crookes A" glass in the light path. It was also found that not all of the radiation passing through the filter cell was absorbed by the "Crookes A" glass and that the per cent. of this infra-red radiation varied for different parts of the image of the arc but was usually 20 to 25% of the total radiation. A second sheet of "Crookes A" glass was found to transmit 75% of the radiation transmitted by the first sheet. The galvanometer deflection corresponding to the three ultraviolet lines can then be calculated by the equation (3–2)—(2–1)/3.

The deflections calculated in this way for the first energy determinations of Expt. 3 are plotted in Fig. 2. The area under this curve is 1826 mm. deflections. The standard lamp when burning on 0.350 ampere gives an energy density of 8.4 ergs per $mm.^2$ per sec. at two meters' distance, and gave under these conditions a deflection of 19.3 cm. at the beginning and 18.9 cm. at the end of the energy determination. The energy density per mm. height of image is therefore $(1826 \times 8.4)/(19.1) = 803$ ergs per sec. The arc is uniformly intense from top to bottom and even if there were slight variations, the thermopile covered most of the height and would have recorded an average energy density. The height of the image was 18.5 mm. which gives as the total energy 803 X 18.5 = 14,860 ergs per sec. There is yet a possible correction due to a greater reflection or absorption of the ultraviolet light as compared to that for the light of the standard lamp by the fluorite window of the vacuum thermopile. The difference in reflection is negligible. There are no data on the absorption of different wave lengths by fluorite, but this is certainly only a small correction and will not be considered.

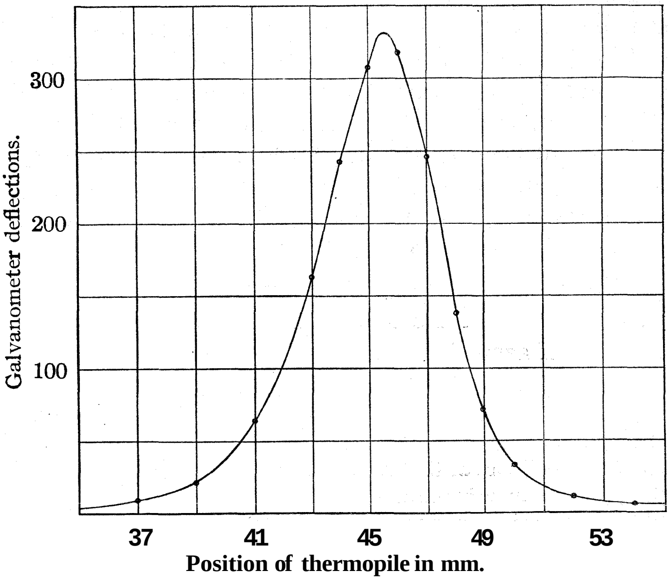

Fig. 2.—Energy distribution curve.

Decomposition of Azomethane

Pour experiments were made at a temperature of 20° and at initial pressures from 0.1207 cm. to 25.74 cm. The pressure measurements of Expts. 1 and 2 were made on a closed tube manometer and in Expts. 3 and 4 a small McLeod gage was used. In all of these experiments the total number of moles decomposed is readily calculated from the total volume and the change in pressure, since it had been shown[2] that the decomposition is largely by the equation $CH_3NNCH_3 = N_2 + C_2H_6$. The final pressure actually is 2.04 times the original pressure, due to a small amount of side reaction. The number of moles decomposed is therefore given by the equation

$$N = \frac{\Delta P V/1.04}{RT}$$

where ΔP is the increase in pressure and V is the total volume.

The volume of the quartz cell was 67 cc. and the connecting tubing to the top of the mercury surface had an average volume of **14** cc. in Expt. **1** and 12 cc. in Expt. 2. The low pressure Expts. **3** and **4** were made with apparatus similar to that used in a previous research.[3] The volume of the cell and the tubing connecting it to the mercury trap was *70* cc., the volume of the trap and tubing connecting it to the McLeod gage was 2.8 cc. and the volume of the gage was 8.9 cc. The total volume was therefore 81 7 cc.

The Fraction of Light Absorbed

The fraction of the light absorbed can be calculated from the absorption coefficient, knowing the length of the cell and the pressure of azomethane in the cell. Diffusion will be sufficiently rapid to give the same partial pressure of azomethane throughout the reaction cell, but practically no diffusion will occur into the tubing leading to the manometer in Expts. 1 and 2. The partial pressure of azomethane will therefore be less in the cell than in the tubing after some decomposition has occurred. Since only a small part of the azomethane was decomposed, this will make very little difference. However, the correct partial pressure of azomethane in the cell is readily calculated. It is given by the equation

$$P_1 = P_i - \Delta P V/V_1 - \Delta P V_2 X_A/1.04 V_1$$

where P_i is the initial pressure, AP the increase in pressure, V the total volume, V_1 the volume of the cell, V_2 the volume of the tubing and X_A the mole fraction of azomethane entering the tubing from the cell.

This is shown as follows. The partial pressure of azomethane in the manometer tubing at any time *t* is given by $P_2 = P_i + \Delta P X_A$. X_A is given with sufficient accuracy by the equation $X_A = (P_i - \Delta P/1.04)/(P_i + AP)$ where *AP* is the average of the total increase in pressure at that reading and the previous reading. Let N_1 represent the moles of azomethane in the cell, N_2 the moles of azomethane in the tubing and N the total moles of azomethane at any time *t*. We have $N_1 = P_1V_1/RT$, $N_2 = P_2V_2/RT$, $N = (P_i - \Delta P/1.04)V/RT$. Also $N = N_1 + N_2$. If now the above value of P_2 is substituted, we obtain the equation given above for P_1. In Expts. **3** and 4 the calculation of the pressure of azomethane in the cell was the same as given in a previous paper:' As formerly, P'_A denotes the pressure of azomethane in the cell before the reading with the McLeod gage was made and P''_A denotes the pressure of azomethane after the reading.[12] The average value of the pressure of azornethane in the cell during each time interval is obtained by averaging the value of P''_A of one reading and P'_A of the next reading. This is the pressure of azomethane upon which the absorption is based.

The absorption coefficient for light of wave length 3660 Å. is found from the curve of Fig. 1 and to be 3.10. This absorption coefficient was checked by use of the thermopile. The cell filled with azomethane gas for Expt. I was placed between the light source and the thermopile. The galvanometer deflection was read, the azomethane was frozen out with liquid air and another reading made. After correcting for the infra-red radiation as in the energy measurements it was found that 63% of the ultraviolet light of the three mercury lines was absorbed. The absorption calcu-

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[12] The equation for P''_{At} given on page 1496 of ref. **3** should of course have read $P''_{At} = P'_{At}\,P''_t/P'_t$.

lated from the absorption coefficient, the length of the cell (9.13 cm.) and the concentration in moles per liter (0.0141), was 60%. Considering the uncertainty of the corrections this is a good agreement. The absorption has been calculated for each time interval and is based on the absorption coefficient, 3.10, and the average concentration of azomethane in the cell.

In addition to the absorption so calculated, a fraction of the light from the two surfaces of the rear window is absorbed. From Fresnel's formula for the reflection of perpendicularly incident light, that is, $r = \left(\frac{n-1}{n+1}\right)^2$, where n is the index of refraction of quartz for $\lambda = 3660$ Å., approximately 12% of the transmitted light is reflected from these two surfaces. The absorption of this reflected light is calculated as before. Secondary reflections are neglected.

The results of the four experiments are given in Table II.

TABLE II

DATA OF FOUR EXPERIMENTS

Expt. 1. Average energy density = 14,480 ergs/sec.

Time, hours	P, cm.	P_1, cm.	Av. P_1, cm.	Moles decomposed × 10^5	Ergs absorbed × 10^{-7}
0	25.74	26.74			
			25.42	2.09	3.26
1	26.23	25.10			
			24.80	1.92	3.22
2	26.68	24.49			
			24.23	1.66	3.17
3	27.07	23.97			
			Total	5.67	9.65
Expt. 2. Average energy density = 14,400 ergs/sec.					
0	9.60	9.60			
			9.42	1.17	1.63
1	9.87	9.25			
			9.09	1.08	1.59
2	10.12	8.93			
			8.77	1.04	1.54
3	10.36	8.62			
			8.46	1.08	1.50
4	10.61	8.30			
			8.17	0.86	1.45
5	10.81	8.05			
			Total	5.23	7.71

Expt. 3. Average energy density = 14,490 ergs/sec.

Time, hours	P, cm.	P'_A cm.	P''_A cm.	Av. P_A, cm.	Motes decomposed × 10^5	Ergs absorbed × 10^{-7}
0	0.991		1.031			
				1.008	0.165	0.217
1.05	1.031	.986	.981			
				.962	.142	.197

TABLE II (*Concluded*)

Time, hours	P, cm.	P'_A cm.	P''_A cm.	Av. P_A, cm.	Moles decomposed $\times 10^6$	Ergs absorbed $\times 10^{-7}$
2.05	1.066	.943	.939			
				.922	.127	.188
3.05	1.096	.904	.901			
				.869	.239	.356
5.05	1.154	.836	.831			
				Total	.673	.958
	Expt. 4.	Average energy density = 13,880 ergs/sec.				
0	0.1207	....	0.1255			
				0.1205	0.0370	0.048
2.00	.1296	0.1155	.1146			
				.1109	.0271	.044
4.00	.1362	.1073	.1067			
				.1029	.0275	.041
6.00	.1429	.0991	.0985			
				.0957	.0215	.033
7.75	.1480	.0928	.0924			
				Total	.1131	.166

The final result to be calculated is the number of molecules decomposed per photon of light absorbed. This number is given by $\phi = h\nu \times$ moles decomposed × 6.06 × 10^{23}/ergs absorbed, where $h\nu$ is the energy in ergs of a photon of light of the wave length λ = 3660 Å. The values of ϕ are as follows.

Expt.	1	2	3	4
ϕ	1.91	2.21	2.29	2.22

Temperature Coefficient

An attempt was made to determine the temperature coefficient of the photochemical decomposition. The absorption 'curve was not appreciably changed at 100°. A very slight deposit was formed on the front window of the reaction chamber. This actually reduced the rate below that at 20°, due probably to the absorption of light by this film. It was found, however, that on changing the gas to 20° the rate in moles decomposed was the same as it was at 100° just before the temperature was changed. Experiments at low pressures would have avoided the difficulty but they were not undertaken owing to lack of time. It seems, however, that the temperature coefficient of the photochemical decomposition is very nearly zero, and certainly not greater than 1.02 for an increase in temperature of 10°.

Discussion of Results

The value of ϕ is practically constant over a 200-fold pressure range and is approximately 2. Expt. 1 is a little lower than the rest, probably because a similar deposit to the one produced at 100° may have formed.

This would be most serious at high pressures and would produce a steady lowering of the rate of decomposition as the experiment progressed, which was actually the case in Expt. 1.

It might be supposed that some molecules would be deactivated by "collisions of the second kind" and that this deactivation would be most serious at high pressures. The constant value of ϕ over this large pressure range would indicate no such deactivation. Either collisions are not effective in deactivating activated molecules, which is not likely, or else they react in a time shorter than the time between collisions at the high pressures. The time between collisions at 25 cm. pressure is about 2 X 10^{-10} seconds if the diameter of the molecule is taken as 6 × 10^{-8} cm.

In the case of thermal decomposition we can calculate the ratio of molecules reacting to molecules deactivated by collisions if we accept Theory II of Rice and the author.[5,6] This ratio is given by b_ϵ/aN, where

$$b_\epsilon = \frac{K_\infty \Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n+1}{2}\right)} \frac{e^{\frac{\epsilon_0}{kT}}}{(kT)^{\frac{1}{2}}} \frac{(\epsilon - \epsilon_0)^{\frac{n-1}{2}}}{\epsilon^{\frac{n-2}{2}}}, \quad a = 4s^2\sqrt{\frac{\pi kT}{m}}$$

and N is the number of molecules per cc. T is taken as 290° to correspond to K = 1.4 X 10^{-4}. For the molecular diameter 6 X 10^{-8} is used. N is calculated for a pressure of 25 cm. and the number of degrees of freedom is 25, this being the value of n required to fit the experimental data; ϵ_0 is 50,600 cal. per mole. If now we take as ϵ 77,800 cal. per mole, which is the energy of a photon of λ = 3660 Å., we get for the ratio 14/1. This calculation does not allow for the internal energy of the molecule before it absorbs the photon. This energy is of course not known, but the average internal energy of all of the molecules is roughly 5,000 cal. per mole, giving ϵ a likely value of 82,800 cal. The ratio then becomes 47/1. The result of this calculation requires that an activated molecule with this very high energy must react within about 10^{-11} seconds after activation. If the type of activation were the same in the photochemical as in the thermal reaction, then deactivation could seldom occur by collision even at the highest pressures, nor could the molecule be deactivated by radiation of the energy, since the time required for radiation is generally more than 10^{-8} sec. The constant value of ϕ over this large pressure range is the expected result if the type of activation and mechanism of reaction were the same in both photochemical and thermal reactions.

The fact that approximately two molecules are decomposed per photon absorbed may possibly be explained by the energy of a newly formed ethane molecule being transferred to a molecule of azomethane which is then activated. This is only possible because of the large excess of energy in the photon and could not be repeated indefinitely, thus producing a long chain. For example, a gram mole may have 83,000 cal. after the photon is absorbed. At least 20,000 cal. is obtained as heat of the reaction itself.[6] This gives more than 103,000 cal. to be divided between a N_2 gram molecule and an ethane gram molecule. The ethane would get by far the larger portion of this energy if statistical equilibrium between the various degrees of freedom of both molecules exists. It must then impart some 60,000 cal. or more to an average azomethane gram molecule to make its reaction probable. Unless the heat of the reaction is very much higher than 20,000 cal., or the energy of surrounding molecules very great, the third molecule of azomethane in such a chain would not have sufficient energy to react, especially if the pressure were high.

Summary

The photochemical decomposition of azomethane has been studied in order to determine the length of the photochemical reaction chain and to test further certain theoretical interpretations of the unimolecular thermal decomposition.

The quantitative absorption curve for ultraviolet light has been determined from 4060 to 2370 Å. There is an absorption maximum at 3390 Å., with increasing absorption again toward the extreme ultraviolet.

The light used for the decomposition consisted of three mercury lines at about 3660 Å., which were isolated by means of a filter. The total energy falling on the reaction cell was determined by means of a thermopile and the fraction of the light absorbed was calculated from the absorption coefficient.

The decomposition was followed by pressure measurements. Four experiments were made at pressures from 0.1207 cm. to 25.74 cm. Two molecules were found to be decomposed for each photon absorbed in all four experiments.

The temperature coefficient was found to be very nearly zero.

On the basis of Theory II of Rice and the author,[5,6] most of the thermally activated molecules having energies corresponding to the average energy of all of the molecules plus the energy of the photon will react even at the highest pressure. Deactivation by collision seldom occurs, because the life of a molecule is less than the time between collisions even at the highest pressure. A constant value of moles decomposed per photon absorbed is the expected result if the mechanisms of the photochemical and thermal reactions are similar.

The decomposition of two moles per photon absorbed may possibly be explained by the transfer of sufficient energy by a newly-formed ethane molecule to an azomethane molecule to cause it to react.

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NOTE

A New Apparatus for Preparing Aluminum Chloride.—For the preparation of a very reactive aluminum chloride, much superior to the ordinary commercial article for the Friedel and Crafts reaction, the apparatus shown and described below has proved entirely satisfactory in this Laboratory. The product, obtained without difficulty as a uniform, fine powder, can be kept with good mechanical stirring in perfect suspension in the reaction mixture and so gives the best possible results.

The apparatus of Pyrex glass[1] may be made to any scale, but the specifications as given will meet all, ordinary laboratory requirements. The tube in which aluminum is heated has a wall thickness of an eighth of an inch, an internal diameter of 1 inch and a length of 22 inches. At one end it is bent at a right angle and expands into a funnel that has a depth of 3.5 inches, a diameter of 3 inches at the bottom and is provided with a quarter-inch ground flange. The latter fits a similar flange on the jar where the product is collected. These surfaces, when thinly coated with vacuum grease, make a tight joint from which vapors do not escape while the reaction is going on. The jar has a diameter of 3 inches, a depth of 4 inches and is equipped with a quarter-inch side-outlet 1 inch below the flange. Such an apparatus is capable of turning out 120 g. of aluminum chloride at a single run. It is not expensive and with reasonable care should last for a long time. The original apparatus has been used in this Laboratory for a great many runs and apparently is as good now as in the beginning.

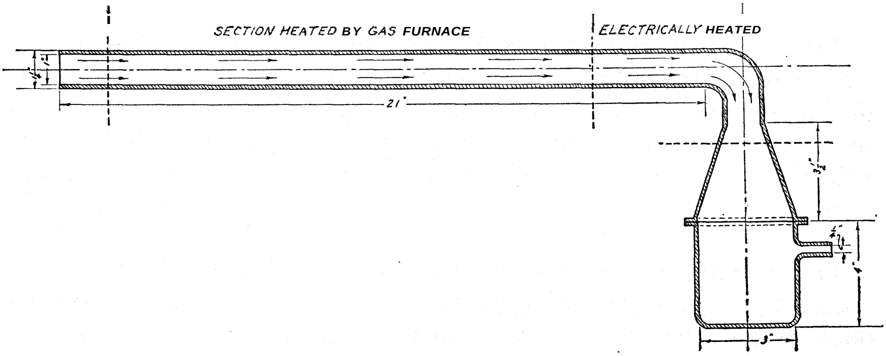

Fig. 1.—An apparatus for making aluminum chloride.

The tube containing the aluminum is heated in a small combustion furnace and the space between the furnace and the top of the funnel is covered with asbestos paper and then wound with 14 feet of 16 gage (B. and S.) nichrome resistance wire. This heating coil is connected with

[1] Supplied by the Corning Glass Company, Corning, New York.

a 110-volt line and the current regulated by a 110 ohm. 7 ampere cage rheostat to produce a temperature of 250" within the tube. The proper setting on the rheostat is determined by a blank trial with a thermometer inside the tube. An asbestos insulation around-the electrically heated area is advisable. Since the receiving jar becomes quite hot during the experiment, it is well to set it in a pneumatic trough filled with water to within a half inch of the outlet-tube. To prevent staining of the heating area, aluminum is introduced into the tube in alundum boats of suitable size.

As soon as air is driven from the system by a rapid stream of dry hydrogen chloride, the flow of gas is checked somewhat and heating is begun at the funnel end by turning on the electric current. The resistance of the rheostat is gradually reduced until at the setting established in the blank trial. The inside of the tube reaches the desired temperature in about half an hour. The furnace burners are then lighted and the stream of hydrogen chloride is increased to its former velocity. At the temperature required for the reaction, white fumes appear in the funnel and settle as a powder on the bottom of the jar. A little of the sublimate collecting on the walls obscures the interior and some escapes through the outlet-tube with the hydrogen. The quantity, however, is negligible. It forms a loose deposit in the outlet-tube and can be easily removed by a stiff wire.

The reaction runs best in a rapid stream of hydrogen chloride at a dull red heat just below the fusion point of aluminum. With these conditions once established, the operation requires little attention. Aluminum chloride is obtained in nearly theoretical yield as an easily removable, white powder. It is at once transferred to the reaction flask, or kept in a desiccator in a tightly closed bottle until needed.

The author wishes to express his thanks to Professors W. H. Warren and B. S. Merigold for advice and assistance in constructing the apparatus and carrying out the process.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE ALCOHOLYSIS AND HYDROLYSIS OF SOME ALKYL HALIDES IN NEUTRAL SOLUTION

BY BEN H. NICOLET AND DONALD R. STEVENS[1]

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It might be not unreasonable to expect that the reactions of alkyl halides would be among the simplest to interpret with which organic chemistry has to deal. The extensive literature of the subject,[2] which cannot be reviewed here shows that this expectation is by no means justified.

A tempting start in the interpretation of these reactions as a class would be to correlate relative reaction rates with polarity of the halogen involved. Now, on the basis of almost any polar theory, one of the striking differences to be expected would be that between primary and secondary halides. For practical purposes the suggested comparison would have to be based on the relative reactivities of propyl and *iso*-propyl iodides, as these constitute the only suitable pair for which any considerable variety of determinations is available.

Propyl iodide reacts more rapidly than isopropyl iodide with sodiomalonic ester, with triethylamine, with sodium ethylate, with sodium phenolate, with sodium benzylate[2] and with sodium thiosulfate.[3] In the case of the chlorides, the same order is observed[4] for reaction with potassium iodide. In fact, with the exception of the work of Brussoff[5] on the velocity of olefin formation with alcoholic potash, which is open to a variety of interpretations, we have found recorded but one reaction in which isopropyl iodide reacts more rapidly than the normal iodide. This is the reaction of the halides with silver nitrate in alcohol solution, studied by Burke and Donnan,[6] who found that the chief change taking place was not ethyl nitrate formation, but alcoholysis of the halide. The reaction was catalyzed both by silver nitrate and silver halide.

The present paper describes measurements of the rate of reaction of the four halides propyl bromide and iodide and *iso*propyl bromide and iodide with ethyl alcohol containing varying small amounts of water. The results may be considered to supplement those of Burke and Donnan in giving a measure of the uncatalyzed alcoholysis. They also permit the calculation of relative rates of hydrolysis under the same conditions.

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[1] The material here presented was used by Donald R. Stevens in partial fulfilment of the requirements for the Ph.D. degree, University of Chicago, August, 1924.

[2] For a partial summary see Haywood, J. *Chem. Soc.*, 121, 1904 (1922).

[3] Slator and Twiss, J. *Chem. Soc.*, 95, 96 (1909).

[4] Conant and Hussey, THIS JOURNAL, 47, 477 (1925).

[5] Brussoff, *Z. physik. Chem.*, *34*, 129 (1900).

[6] (a) Burke and Donnan, *J. Chem. Soc.*, 85, 555 (1904); (b) Z. physik. Chem., 69, 148 (1909).

Experimental Part

An accurately weighed portion of the halide was dissolved in sufficient alcohol of the chosen concentration to give 150 cc. of solution. The solutions were 0.33–0.35 molar. This solution was now transferred to the reaction flask, which contained 4 g. of powdered calcium carbonate,[7] and rapidly heated to boiling under efficient reflux. At the end of chosen periods, usually 2, 4, 6, 8 and 10 hours, samples were removed, cooled to 25° and suitable volumes measured for analysis.

For the analysis the samples were submitted to rapid steam distillation until all of the organic halide was removed and the non-volatile halide was then titrated by the Volhard method with *N*/30 silver nitrate.

Due to the large excess of alcohol, and in most cases of water also, which was present, velocity constants were calculated by the usual equation for reactions of the first order. The K so obtained is a combination of the constants of the two competing reactions, hydrolysis and ethanolysis. A typical run is illustrated in Table I.

TABLE I

RESULTS OF A TYPICAL RUN

Isopropyl iodide (*0.330 M*) in 96.08%[a] alcohol

Time, hours	% Reaction	$K \times 10^3$ (hours)
2	4.9	25.1
6	14.4	26.0
8	18.8	26.1
10	23.2	26.4
	Average	25.9
	Average variation	0.4

[a] All alcohol concentrations are in per cent. by weight.

The variation in the constants calculated for other runs was approximately the same as for the one shown. For the sake of brevity, the remaining series of experiments on the four halides are represented in Table II only by the average values of K obtained in similar runs. The columns headed "% reaction (10 hours)" is included to show how far the reaction had progressed at the time measurements ceased. Laboratory regulations made it impracticable to continue the runs for longer periods.

Discussion of Results

The assumption that two reactions, hydrolysis and alcoholysis, are involved, and that these alone take place, requires some justification. This is found, primarily, in the degree of agreement (shown in the last three columns of Table II) between observed values of K and those calculated

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[7] The calcium carbonate was necessary to prevent the accumulation of halogen acids in the solution. Without it there was definite evidence of the disappearance of HBr or HI by reaction with the solvent alcohol. The constancy of the results obtained indicates that the carbonate caused no serious disturbance. While its use had the theoretical disadvantage that water was formed in the solution ($CaCO_3 + 2HX = CaX_2 + H_2O + CO_2$) during the reaction, calculation will show that the effect was quantitatively of little importance under the conditions actually employed.

TABLE II

REACTION RATES OF ALKYL HALIDES IN NEUTRAL ALCOHOL

Water, % by wt. in alcohol	% Reaction (10 hours)	$K \times 10^3$ (hours), found	$K \times 10^3$ (hours), calcd.	Diff., %
Isopropyl iodide (0.330 M)				
0.15	16 22	17.4	17.44	0.2
1.05	18.39	19.7	19.5	−1.0
1.73	...	20 8	21.06	1.2
3 92	23.20	25.9	26 06	0.6
9 85	34 04	39.8	39.75	−0.1
$Ka = 17.1 \times 10^{-3}$		$Kw = 246 \times 10^{-3}$		
Propyl iodide (0.339 M)				
1.12	5 75	5.88	5.85	−0 6
1 92	6.06	6.18	6.25	1.1
2 68	...	6.66	6.63	−0.4
7.84	8.83	9.23	9.22	−0.1
$Ka = 5.28 \times 10^{-3}$		$Kw = 55.6 \times 10^{-3}$		
Isopropyl bromide (0.355 M)				
0.74	7.06	7.31	7.33	0.3
2 04	8.17	8.47	8.50	0.3
2.92	8.89	9.19	9.29	1.0
7.84	13.05	13.84	13.71	−1.0
$Ka = 6.66 \times 10^{-3}$		$Kw = 96.7 \times 10^{-3}$		
Propyl bromide (0.365 M)				
0.35	4.13	4.19	4.19	0.0
1.12	4.39	4 47	4.56	2.0
2.50	5 35	5.40	5.21	−3.5
7.55	...	7.49	7.61	1.6
$Ka = 4.03 \times 10^{-3}$		$Kw = 51.3 \times 10^{-3}$		

when it was assumed (see above) that the observed rates were made up of two linear components proportional, respectively, to the concentrations of alcohol and of water present in each series.

The reaction of alcoholysis involves ether formation. In the experiments tabulated, the isolation of the ethers would have been excessively difficult and their quantitative determination practically impossible. A special experiment, in which a larger proportion of iso-amyl iodide was refluxed for several days with absolute alcohol containing an excess of calcium carbonate, did however result in the isolation of several grams of *iso*-amylethyl ether. The reaction of alcoholysis does, then, take place under such conditions as have been employed. We have not attempted as yet to show the absence of olefin formation under these conditions but we do not know of any case in which this reaction has been observed in dilute, essentially neutral solutions.

Again, the use of the equation for a reaction of the first order in calculating the results given appears at first sight anomalous. In the most extreme case (line 1, Table II) the solution contained 0.330 mole of isopropyl iodide and only 0.065 mole of water. It contained, however, 17.0 moles of alcohol, and the proportion of isopropyl iodide reacting with water to that reacting with alcohol in any given time would thus have been (see values of Ka and Kw and discussion below) $(0.246 \times .065)/(0.0171 \times 17.0) = 0.67$. As the amount of isopropyl iodide which had reacted at the close of the experiment was $0.1622 \times 0.330 = 0.0536$ mole, the amount reacting with water would have been $0.0536 \times 0.057 = 0.0036$ mole, or 5.6% of the water present. As this is much the most extreme case of low water concentration considered, the policy of neglecting changes in the concentration of water during reaction is thought to be justified.

The values of K obtained with a given halide, when plotted against the water content of the alcohol used, fall near a straight line which may be represented by the equation

$$A + B \text{ (wt. fraction water)} = K$$

Here A and B are constants. Table II shows the calculated values of K determined from such a straight line. If Ka and Kw represent the respective constants for the reactions due to alcoholysis and hydrolysis, then the equation may also be written

$$Ka \text{ (wt. fraction alcohol)} + Kw \text{ (wt. fraction water)} = K$$
$$\text{Here } Ka = A \text{ and } Kw = Ka + B$$

The values of Ka and Kw thus derived are included in Table II. Ka should represent with some accuracy the value of K for 100% alcohol. Kw is rather less accurate and may bear little relation to the rate which would be found in pure water. The ratios of the values of Kw obtained for the different halides should, however, be more significant.

Attention is called to the fact that the rate of reaction found is in each case greater for the secondary halides. The ratio of Ka for isopropyl iodide to that for propyl iodide is 3.24; for the bromides this ratio is 1.65. Similar ratios of Kw are 4.42 for the iodides and 1.89 for the bromides. It is certainly a remarkable fact that the secondary halides react the more rapidly in neutral solution and yet the less rapidly in alkaline solution.[2] Pending further data, no explanation is here offered. It is, however, of interest to note that the rate ratios found are greater in the case of the iodides. If the polarities of the halogen atoms are responsble for the variations in rate, one would expect to find the divergence widest in the case of the iodides, since iodine is a less definitely negative element than bromine and should thus be capable of showing a greater variation in polarity under a given stimulus.

Corresponding to the catalytic effect of silver salts reported by Burke and Donnan, it was found that the alcoholysis of the halides studied was markedly catalyzed by the corresponding mercuric halides. Thus 0.34 molar isopropyl bromide reacts some 20 times as rapidly in the presence of 0.17 molar mercuric bromide, and the influence of dissolved mercuric iodide on the reaction of isopropyl iodide was even greater. Satisfactory constants have not as yet been obtained, but the catalyst appears to be inactivated according to the equation $HgX_2 + 2X^- = HgX_4^{--}$.

Summary

1. The rates of alcoholysis and hydrolysis of propyl and isopropyl bromides and iodides in boiling alcohol containing definite small amounts of water have been measured.
2. The reactions considered differ from most of those which have been studied with alkyl halides in that the secondary halides show in each case a more rapid reaction than the corresponding primary halides.
3. The reactions are strongly catalyzed by the corresponding mercuric halides.

CHICAGO, ILLINOIS

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

ANOMALOUS EFFECT OF ORTHO-PARA ORIENTING GROUPS ON THE MELTING POINTS OF DIHALOGENATED BENZENE DERIVATIVES

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Introduction

The introduction of an additional substituent into the benzene nucleus usually results in the formation of a compound which has a higher melting point than the parent substance. For this reason the observation that symmetrical tribromobenzene has a somewhat higher melting point than its amino derivative led to a study of the melting points of halogenated benzenes and their derivatives. The investigation showed that the melting points of derivatives of halogenated benzene increased with the number of substituents in the nucleus, except in the case of those compounds which are formed by the entrance of a group which causes ortho-para substitution into a para halogenated benzene.

Symmetrical chloro-bromo-iodobenzene and its amino derivatives were prepared in order to show the effect of the introduction of the amino group on the melting points of the trihalogenated benzenes.

Study of the Melting Points

An examination of the melting points of the disubstituted halogen benzene derivatives showed that the amines of the ortho and meta halogen derivatives melted at a higher temperature than the corresponding dihalogenated benzene, whereas the melting points of the amino derivatives of para halogenated benzene are lower. In a similar way the melting point of a derivative of an ortho or meta dihalogenated benzene is raised when a halogen or a methyl group instead of an amino group enters the molecule while that of the para compound is lowered.

On the other hand, when a nitrile group replaces a hydrogen of a dihalogenated benzene, the melting point of the para as well as those of the ortho and meta compound is raised. The fact that the nitrile group had a different effect from the amino, halogen and methyl groups seemed to indicate that substituents which caused the formation of meta disubstituted derivatives of benzene raise the melting points of all three types of dihalogen benzene derivatives upon entering the molecule, while those groups which cause the formation of ortho and para derivatives of benzene raise the melting points of ortho and meta halogenated benzene but lower that of the para when a trisubstituted benzene derivative is formed.

A further examination of the effect of other groups which cause meta substitution showed that they had the same effect as the nitrile group.

The data are given in tabular form below.

TABLE I

EFFECT OF A THIRD SUBSTITUENT ON THE MELTING POINTS OF DIHALOGENATED BENZENES

ND—No substituted dihalogenated benzene derivative is described.
+ Melting point of the dihalogenated benzene is raised on substitution.
− Melting point of the dihalogenated benzene is lowered on substitution.

Groups present		Groups entering	Ortbo deriv.	Meta deriv.	Para deriv.
Cl	Cl	I	ND	ND	−
Cl	Cl	Br	+	+	−
Cl	Cl	Cl	+	+	−
Br	Br	Cl	+	+	−
Br	Br	Br	+	+	−
Br	Br	I	ND	+	−
I	I	I	ND	+	−
Cl	Cl	OH	+	+	+
Br	Br	OH	+	+	ND
I	I	OH	+	+	−
Cl	Cl	CH3	Liq.	Liq.	−
Br	Br	CH_3	+	+	−
I	I	CH_3	+	+	ND
Cl	Cl	NH_2	+	+	−
Br	Br	NH_2	+	+	−
I	I	NH_2	+	+	−
Cl	Br	NH_2	+	+	−
Cl	I	NH_2	+	+	ND
Br	I	NH_2	+	+	ND
Cl	Cl	CN	ND	+	+
Br	Br	CN	ND	+	+
Cl	Cl	NO_2	+	+	+
Br	Br	NO_2	+	+	−
I	I	NO_2	+	+	−
Cl	Br	NO_2	+	+	+
Cl	I	NO_2	ND	+	+
Cl	Cl	SO_3H	ND	ND	+
Br	Br	SO_3H	+	+	+
Cl	Cl	CHO	+	+	+
Cl	Cl	COOH	+	+	+
Br	Br	COOH	+	+	+
Cl	Br	COOH	+	+	+

The table shows that none of the iodo derivatives of o- or *m*-dichlorobenzene are described in the literature, but that the iodo derivative of *p*-dichlorobenzene has a lower melting point than that of p-dichlorobenzene. The + or − signifies that the melting points of all of the isomers described in the literature, which are formed by the entering group, have a higher or lower melting point, respectively, than that of the parent dihalogenated benzene.

From the table we may make the following generalizations.

1. The melting point of an ortho or meta disubstituted halogen derivative is raised by the entrance of a third group. This has been found to hold for the substitution of a chlorine, bromine or iodine atom or an hydroxyl, methyl, amino, nitrile, nitro, sulfonic acid or carboxyl group.

2. The melting point of a para disubstituted halogen derivative is raised by the entrance of a third substituent if the group entering is one which causes meta substitution.

3. The melting point of a para disubstituted halogen derivative is lowered by the entrance of a third substituent if the group entering is one which causes ortho-para substitution.

It can be seen that there is no exception to rule number 1; two exceptions to rule number 2 (1-nitro-2,5-dibromobenzene and 1-nitro-2,5-di-iodobenzene melt lower than the corresponding dihalogenated derivatives); and one to rule 3 (1-hydroxy-2,5-dichlorobenzene melts 4 degrees higher than the dihalogenated benzene). The three compounds having melting points which were exceptions to rules 2 and 3 were prepared and their melting points were found to agree with those given in the literature.

It should be noted that Holleman[1] and Francis and co-workers[2] have shown that the —NO_2 group has less meta directing influence than the —SO_3H group, and this less than the —COOH group. Nitro compounds offer the only exception to rule 2.

The reason for the lowering of the melting points of the para dihalogenated benzenes by the entrance of certain groups is not clear. It is known that the amino group, for instance, has a strong effect on the ortho and para positions and it was thought that this lowering might be due to the influence of the entering amino group on the halogen it finds ortho or para to it. In that case, however, we should expect that any trisubstituted benzene derivative in which the amino group was ortho or para to a halogen would have a lower melting point than the corresponding dihalogen derivative; but this is not true. It is only when the halogens are para to each other that the amino or similar group has this property.

An examination of the melting points of the trisubstituted amines shows that, in, general, the melting point of the trisubstituted benzene compound is lower than that of the corresponding trisubstituted aniline with the exception of symmetrical tribromo-aniline and 3,4,5-tri-iodo-aniline. In the latter compounds the corresponding amine has a lower melting point than the trihalogenated benzene. Inasmuch as the trisubstituted aniline derivatives containing chlorine, bromine and iodine in the same molecule were not known it seemed worth while to prepare them and note the relation of their melting points to the parent trisubstituted hydrocarbon.

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[1] Holleman, *Chem. Reviews*, 1,202 (1924).

[2] Francis, Andrews and Johnston, THIS JOURNAL, 48,1625 (1926).

It was found in each case that the amine melted at a higher temperature than the corresponding trihalogenated benzene.

A search for the dielectric constants and refractive indices of the compounds whose melting points have been studied was made, to see whether there was a corresponding difference in these constants for the para halogenated benzene derivatives, but sufficient data from which to draw conclusions could not be found.

Compounds which have small external fields of force should have lower melting points than similar compounds having larger fields of external force. Inasmuch as compounds having larger external fields of force should be more reactive than those having a smaller field of force, it would seem that the trisubstituted derivatives formed from ortho and meta compounds by substituting an ortho-para orienting group should be more reactive than the trisubstituted derivative formed from the para compound. This phase of the problem will be further investigated.

There are some indications that the lowering of the melting point of para disubstituted benzene derivatives by the introduction of groups causing ortho-para substitution holds for other than the halogen compounds.

Experimental

A sample of each compound whose melting point was to be determined was placed in a vacuum desiccator over concd. sulfuric acid and was allowed to remain under a pressure of 25 mm. for at least twenty minutes to remove traces of the solvent. The melting point was determined by immersing a capillary tube containing the sample in a bath of concentrated sulfuric acid about 10° below the melting point of the compound. The acid was agitated by means of a ring stirrer while the temperature was very gradually raised.

For the preparation of the three amines of symmetrical trihalogenated benzene, *p*-bromo-acetanilide, p-chloro-acetanilide and *o*-chloro-aniline were used. To prepare 2-chloro-4-bromo-6-iodo-aniline, *p*-bromo-acetanilide was chlorinated by means of HOCl according to the method of Chattaway and Orton,[3] producing 2-chloro-4-bromo-acetanilide. This anilide was then saponified and iodine was introduced into the benzene nucleus by using iodine monochloride. The amine was dissolved in acetic acid and the vapors of iodine monochloride were passed into the solution. The iodine monochloride was prepared according to the method of Jackson and Whitmore.[4]

The 2-bromo-4-chloro-6-iodo-aniline was prepared in a similar manner, starting with p-chloro-acetanilide. The bromine was introduced into the benzene ring by the method of Mannino and Di Donata.[5] In this method bromine formed by the action of nitric acid on hydrobromic acid reacts with the anilide.

In attempting to prepare 2-chloro-4-iodo-6-bromo-aniline it was found that iodine monochloride reacted with o-chloro-aniline to form products which had a much higher melting point than that of 2-chloro-4-iodo-aniline. This compound had been previously prepared by Dains, Vaughan and Janney[6] and was found to melt at 70–71°.

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[3] Chattaway and Orton, Ber., 33, 2398 (1900); *J. Chem. Soc.*, 79, 274–280 (1901).

[4] Jackson and Whitmore, THIS JOURNAL. 37, 1528 (1915).

[5] Mannino and Di Donata, *Gazz. chim. ital.*, [2] 38, 24 (1908).

[6] Dains, Vaughan and Janney, THIS JOURNAL, 40,933 (1918).

The 2-chloro-4-iodo-aniline was prepared from o-chloro-aniline by refluxing with iodine, water and ether, according to the directions given by Dains, Vaughan and Janney[6] and was then brominated by dissolving in acetic acid and adding bromine.

The three amines were diazotized using alcohol, sodium nitrite and sulfuric acid. The same trisubstituted benzene was obtained in each case; thus proving that the amino derivatives were symmetrical trihalogen anilines.

Action of ICl on 2-Chloro-4-bromo-acetanilide

One g. of the 2-chloro-4-bromo-acetanilide, m. p. 150–151°, prepared by the general method of Chattaway and Orton,[3] was dissolved in acetic acid and ICI vapor passed into the solution. Upon the addition of water, 0.7 g. of a white precipitate was formed, which proved to be unchanged **2-chloro-4-bromo-acetanilide.** The small amount remaining in the mother liquor was discarded.

Saponification of 2-Chloro-4-bromo-acetanilide

Eight and seven-tenths g. of the **2-chloro-4-bromo-acetanilide** was refluxed with 6.1 g. of potassium hydroxide dissolved in 75 cc. of alcohol for about eight hours. The alcohol was distilled off on the steam-bath and water added. The amine was filtered from the cold solution, washed with cold water and crystallized from petroleum ether; b. p. 100–115°. Six and one-tenth g. of product having a melting point of 70–71° was obtained, which corresponds to an 84.6% yield.

Direct Iodination of 2-Chloro-4-bromo-aniline

The direct iodination of 2-chloro-4-bromo-aniline was carried out following the procedure of Wheeler and his co-workers.[7]

One g. of the amine gave a black tar which was subsequently discarded, and 0.3 g. of 2-chloro-4-bromo-6-iodo-acetanilide. The melting point was 97–97.5° after crystallizing from petroleum ether; yield, 18.6%. The product was identical with that obtained by **the** action of ICl on 2-chloro-4-bromo-aniline.

Preparation of 2-Chloro-4-bromo-6-iods-aniline

One g. of the amine was dissolved in about 20 cc. of glacial acetic acid and sufficient water was added so that the mixed solvent was nearly saturated with the amine. **One g.** of ICl vapor was blown into the solution, and a light-colored, crystalline precipitate settled out. The precipitate was dissolved in the mother liquor by warming and then allowed to crystallize. One and three-tenths g. of 2-chloro-4-bromo-6-iodo-aniline was obtained, m. p. 94–95', corresponding to a yield of 81%. On recrystallizing from petroleum ether, a product melting at 97–97.5° was obtained. Further crystallizations from alcohol by the addition of water, and from ethyl acetate by the addition of petroleum ether failed to change the melting point.

Anal. Subs., 0.5064: N_2, 21.2 cc. at 24°; 743.1 mm. (corr.) collected over 23.1% KOH. Calcd. for $C_6H_4NClBrI$: 4.21. Found: 4.59.

Preparation of 2-Bromo-4-chloro-6-iodo-aniline

2-Bromo-4-chloro-acetanilide was prepared from 4-chloro-acetanilide by the method of Mannino and Di Donata[5] and converted to the corresponding amino compound by saponification. One g. of the 2-bromo-4-chloro-aniline was dissolved in 20 cc. of acetic acid and water added until the solution became turbid. One g. of ICl vapor was then blown into the solution. One and six-tenths g. of crude 2-bromo-4-chloro-6-iodo-aniline

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[7] Wheeler and others, *Am. Chem. J.,* 42,441461 (1909); 44,127,493–507 (1910).

precipitated. The crude material was crystallized from petroleum ether; 1.5 g. having a melting point of 109.5–110° was obtained, corresponding to a 93.3% yield.

Anal. (semi-micro). Subs., 0.0475 g.: N_2, 1.92 cc. at 21°; 737 mm. (corr.) collected over 33% KOH. Calcd. for $C_6H_4NClBrI$: 4.21. Found: 4.48.

This analysis was carried out according to an unpublished method of Lauer and Sunde.

Preparation of 2-Chloro-4-iodo-6-bromo-aniline

Method A. By Bromination of 2-Chloro-4-iodo-aniline

Seven and seven-tenths g. of 2-chloro-4-iodo-aniline, prepared according to the directions of Dains, Vaughan and Janney[6] was dissolved in 35 cc. of glacial acetic acid and 5 g. of bromine was added. The reaction mixture warmed up and after a little while crystals began to appear. These were filtered off and water was added. Eight and five-tenths g. of crystals were obtained which had a constant melting point of 115.5–116° after 2 crystallizations from alcohol. Recrystallizing from petroleum ether failed to change the melting point. The yield was 84.2% of the calculated.

Anal. (semi-micro). Subs., 0.0223 g.: N_2, 0.77 cc. collected over 33% KOH at 26°; 759.3 mm. (corr.). Calcd. for $C_6H_4NClBrI$: 4.21. Found: 4.04.

Method B. By the Chlorination of 2-Bromo-4-iodo-acetanilide

Six g. of finely ground *p*-iodo-acetanilide was brominated according to the general method of Mannino and Di Donata.[5] Seven and two-tenths g. of the pure anilide was obtained, melting at 140–140.5° after crystallizing from alcohol; yield, 92.3%.

Anal. (semi-micro). Subs., 0.0320 g.: N_2, 1.21 cc. at 22° and 737.2 mm. (corr.) over 33% KOH. Calcd. for C_8H_7ONBrI: 4.12. Found: 4.18.

One and eighty-five hundredths g. of 2-bromo-4-iodo-acetanilide was saponified and treated in the usual manner. One and four-tenths g. of the amine which melted at 77.5–78° after crystallizing from petroleum ether was obtained; yield, 70.4%. A small portion of the amino compound was converted to the anilide by treatment with acetyl chloride. The melting point was 139–140°, thus proving the identity of the positions before and after saponification. The picric acid addition compound melted at 125°.

The 2-bromo-4-iodo-aniline was converted to 2-bromo-4-iodo-6-chloro-aniline by dissolving in glacial acetic acid and adding the calculated amount of chlorine dissolved in glacial acetic acid. A white precipitate having a high melting point was immediately formed. On filtering and adding water, the trihalogenated aniline was obtained. It was crystallized from alcohol and from petroleum ether. A mixed melting point proved its identity with the 2-bromo-4-iodo-aniline obtained by brominating 2-chloro-4-iodo-aniline.

Preparation of *Sym.*-chloro-bromo-iodo-benzene

1. Diazotization of 2-Iodo-4-chloro-6-bromo-aniline

Forty-one hundredths g. of 2-iodo-4-chloro-6-bromo-aniline was refluxed for half an hour on a steam-bath with 1.64 cc. of ethyl alcohol, one and six-tenths cc. of concd. sulfuric acid and 1.1 g. of sodium nitrite. The mixture was then diluted and the reddish precipitate which separated was thoroughly washed and finally dried in a vacuum desiccator. Thirty-five hundredths g of product was obtained which melted at 85.5–86° after 2 crystallizations from alcohol. The yield was 89.5%.

2. Diazotization of 2-Chloro-4-bromo-6-iodo-aniline

Six-tenths g. of this amine was refluxed for half an hour with 0.14 g. of sodium nitrite, 2.5 cc. of ethyl alcohol and 1 cc. of concd. sulfuric acid. The mixture was then diluted with water and the reddish colored oil which soon solidified was thoroughly washed with water. After drying in a vacuum desiccator **0.55** g. of product was obtained which after two crystallizations from alcohol melted at 85.5–86°. The red color was removed by boiling the alcohol solution with a little Norit. A yield of 96.2% was obtained.

3. Diazotization of 2-Chloro-4-iodo-6-bromo-aniline

To **2.15** g. of the amine was added **0.5** g. of sodium nitrite, **3.5** cc. of concd. sulfuric acid and **10** cc. of ethyl alcohol. After refluxing for half an hour and evaporating the alcohol, the residue was steam distilled. One and five-tenths g. of a white crystalline substance was obtained from the distillate on cooling. After one crystallization from alcohol, the substance melted at 85.5–86.0°. The yield was **73.2%.**

Mixed melting points of the halogenated benzenes obtained from the three trisubstituted anilines showed that the products were identical. The fact that the three amines gave the same compound on diazotization proves the symmetrical arrangement of the halogens.

Summary

1. A study of the melting points of halogenated benzene derivatives shows that the melting points are raised by the introduction of additional groups except in the case of one class of compounds. Contrary to the general rule, the melting points of para dihalogenated benzene derivatives are lowered by the introduction of a group causing ortho-para substitution.

2. Symmetrical trihalogenated benzene derivatives containing iodine, bromine and chlorine in the same ring have been prepared for the first time.

3. The amino derivatives of these compounds have higher melting points than the parent hydrocarbons.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

ACTION OF THIONYL CHLORIDE ON ORGANIC ACIDS[1]

BY L. MCMASTER AND F. F. AHMANN

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Thionyl chloride is a reagent which has become very important for the synthesis of a large variety of organic compounds. In a recent article by Silberrad,[2] a summary of the work upon thionyl chloride is given. It is mentioned as a chlorinating and dehydrating agent, as a reagent for the removal of hydrogen from mercaptans, as a condensing agent and as a catalyst. The most frequent use of this reagent is for the conversion of an acid into its chloride, since it is easier to handle than phosphorus pentachloride. This investigation was begun some months previous to the review by Silberrad and had for its object a systematic study of the reaction of thionyl chloride on organic acids.

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[1] This paper was presented before the Division of Organic Chemistry of the American Chemical Society, Richmond, Virginia, April **11** to 16, **1927.**

[2] Silberrad, J. *Soc. Chem. Ind.*, **45,** 37, 55 **(1926).**

Experimental Procedure

Pure acids in quantities of 15 to 25 g. were treated with two or three times their weight of pure thionyl chloride. In some cases the reaction took place immediately but usually the mixture had to be refluxed with stirring at the boiling point of the thionyl chloride to complete the reaction. In a few cases several days' refluxing were required. In most cases the acid dissolved in the thionyl chloride and a solvent was unnecessary. When a solvent was required, benzene, ether, petroleum ether, gasoline, pyridine and other inert solvents were tried. Since the by-products of the reaction are gaseous, they were readily removed and any excess thionyl chloride was distilled off. Usually the thionyl chloride replaced the OH group by Cl, forming an acid chloride, but in some cases with the dibasic acids anhydrides were formed. These products were purified either by vacuum distillation or by crystallization. In cases where acids were found not to react, various catalyzers such as pyridine, aluminum chloride and iodine were tried.

TABLE I

SUBSTITUTED ACETIC ACIDS

Acid	Amt. in g.	Time, hours	Product	% Yield
Chloro-acetic	15	24	Monochloro-acetyl chloride	55
Trichloro-acetic	15	48	None	..
Amino-acetic	12	12	None	..

The three negative chlorine groups in trichloro-acetic acid evidently prevent the formation of an acid chloride. With the amino-acetic acid a reaction took place and the thionyl chloride turned intensely red but we were unable to isolate any products of the reaction. It is probable that the amino group was attacked.

TABLE II

ALIPHATIC DIBASIC ACIDS

Acid	Amt. in g.	Time, hours	Product	% Yield
Oxalic	15	72	None	..
Malonic	15	2	Malonyl chloride	60
Succinic	20	6	Succinic anhydride	78
Glutaric	15	6	Glutaric anhydride	78

It was thought that thionyl chloride might react with diethyl oxalate to form oxalyl chloride, but no reaction took place upon refluxing the mixture for forty-eight hours. This is the only method by which malonyl chloride can be prepared, since phosphorus pentachloride converts malonic acid into carbon suboxide. It is a liquid which distils at 55° (15 mm.) and turns dark red on standing. The literature records that succinic anhydride can best be made by this method. Suberic and sebacic acids are reported[3] as forming dichlorides.

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[3] Hans Meyer, Monatsh., 22, 415, 777 (1901).

The Hydroxy Acids

The action of this reagent on the hydroxy acids has not been studied very extensively. Malic acid is mentioned as forming a dichloride, while no reference is made to tartaric acid. Lactic acid yields a variety of products.[4] Tartaric acid is the only one of this group studied by us. 15 g. of the acid was refluxed for several days with 40 cc. of thionyl chloride without any result. No suitable solvent for the acid could be found in which to carry out the reaction.

Unsaturated Dibasic Acids

Fumaric, mesaconic and bromomaleic acids are described3 as forming dichlorides, while maleic, citraconic and itaconic acids form anhydrides. We obtained a 90% yield of maleic anhydride but could not get fumaric acid to react. Benzene, petroleum ether and pyridine were used as solvents without success. We intend to repeat the action of thionyl chloride on the other unsaturated dibasic acids mentioned, since our work does not agree with the results given in the literature.

TABLA III

SUBSTITUTED BENZOIC ACIDS

15 g. of acid used in each case

Acid	Time, hours	Product	% Yield
o-Nitrobenzoic	3	o-Nitrobenzoyl chloride	90
m-Nitrobenzoic	3	m-Nitrobenzoyl chloride	86
p-Nitrobenzoic	6	*p*-Nitrobenzoyl chloride	73
o-Aminobenzoic	3	None	..
m-Aminobenzoic	3	m-Aminobenzoyl chloride	83
p-Aminobenzoic	4	*p*-Aminobenzoyl chloride	88

Heumann and Koechlin[5] studied the action of thionyl chloride on benzoic acid. We obtained a 98% yield against one of 90% by the phosphorus pentachloride method. Meyer[6] has prepared by this method the p-nitrobenzoyl chloride after a long period of refluxing. We found that it was the most difficult of the three to prepare.

Phosphorus pentachloride cannot be used to prepare an acid chloride of an aminobenzoic acid since it attacks the amino group. We could find no references to the acid chlorides of the aminobenzoic acids. In the case of the o-aminobenzoic acid a vigorous reaction took place when it was first treated with the thionyl chloride and it was necessary to surround the flask with a freezing mixture. We were not able to isolate any definite products of the reaction. The *m*-aminobenzoyl chloride is a yellow oil distilling at 125° (15 mm.). Upon standing it passes into a solid of m. p. 42° and possesses a decided acid chloride odor. It reacts vigorously with

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[4] Frankland and Garner, J. Chem. *Soc.*, 105, 1101 (1914).

[5] Heumann and Koechlin, Ber., 16, 1625 (1883).

[6] Hans Meyer, J. Chem. *Soc.*, 80, 1, 628 (1901); 82, 1, 31 (1902).

water, ammonia and alcohol. Analysis gave 22.72% of chlorine whereas the calculated value is 23.44%. The *p*-aminobenzoyl chloride is also a yellow oil distilling at 120° (12 mm.), solidifying upon standing to yellow crystals of m. p. 31°. These crystals possess the same properties as the meta compound and were found to contain 22.62% of chlorine.

The Hydroxybenzoic Acids

In only exceptional cases have the acid chlorides of the hydroxybenzoic acids been prepared by ordinary methods. When phosphorus pentachloride is used as a chlorinating agent, the OH group is also attacked. Meyer found that salicylic acid, m-hydroxybenzoic acid and *o*-and *m*-cresotinic acids readily formed the acid chlorides with thionyl chloride. We were able to obtain by using the free acid only a very small yield of the acid chloride of salicylic acid but a **36%** yield was obtained by using the sodium salt of the acid. The salicylyl chloride is a white, crystalline substance melting at 18° to a colorless, sirupy liquid which distils at 90° (11 mm.). No yield of the acid chloride could be obtained with m-hydroxybenzoic acid nor with o-and m-cresotinic acids as claimed by Meyer. We obtained only glassy solids of indefinite composition. The para acids do not react. Meyer states that an acid chloride is not formed if the acid has an OH group in the para position unless a second OH group is in the ortho position with respect to the first OH group.

The Phthalic Acids

The phthalic acids have been studied previously by Meyer, who found that phthalic acid formed an anhydride, isophthalic acid a dichloride and terephthalic acid was unattacked. Since no yields were recorded they were reinvestigated.

TABLE IV

THE PHTHALIC ACIDS

Acid	Amt. in g.	Time, hours	Product	% Yield
Phthalic	20	2	Phthalic anhydride	95
Isophthalic	10	12	Isophthalyl chloride	62
Terephthalic	15	72	None	..

Attempts to prepare phthalyl chloride were made by prolonged boiling of the anhydride with the thionyl chloride using aluminum chloride, iodine and pyridine as catalysts but without success. The isophthalyl chloride is a colorless oil distilling at 200° (15 mrn.). Catalyzers and various inert solvents were tried in the attempt to prepare terephthalyl chloride.

Summary

1. Thionyl chloride readily converts the acids of the fatty acid series into acid chlorides. Chloro-acetic acid is converted into an acid chloride while trichloro-acetic and amino-acetic acids are not.

2. Of the dibasic acids, oxalic is unattacked, while succinic and glutaric yield anhydrides and malonic, suberic and sebacic acids form dichlorides.

3. Tartaric acid is unattacked.

4. Of the unsaturated dibasic acids employed, maleic forms an anhydride and fumaric acid is unchanged.

5. Of the benzoic acids, the three nitrobenzoic acids all form the acid chlorides. The p-nitrobenzoyl chloride is formed only with difficulty due to the presence of the negative nitro group in the para position. Acid chlorides of m-and p-aminobenzoic acid can be prepared by this method. The ortho acid does not form an acid chloride.

6. Only by the use of thionyl chloride can the acid chlorides of some of the aromatic hydroxy acids be prepared. o-Hydroxybenzoic acid forms an acid chloride while the para acid does not. m-Hydroxybenzoic acid and the cresotinic acids gave products which could not be identified as acid chlorides as stated by Meyer.

7. Of the phthalic acids, the ortho acid forms an anhydride, the meta acid a dichloride and the para acid is not attacked by thionyl chloride.

8. The action of thionyl chloride on other organic acids is being continued in this Laboratory.

St. Louis, Missouri

[Contribution from the Chemical Laboratory of Princeton University]

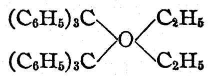
THE HEXAPHENYLETHANE ALKYL SULFIDE ADDITION COMPOUNDS[1]

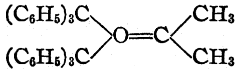
By Victor C. Rogers[2] and Gregg Dougherty

Received June 27, 1927 Published January 5, 1928

Introduction

Hexaphenylethane (triphenylmethyl) possesses the property of forming addition products with a great variety of organic substances.[3,4] The majority of these addition products have a composition corresponding to the ratio of one mole of hexaphenylethane to one mole of the substance added. In the case of the additions involving esters, ethers and ketones,[5] the oxonium theory is probably applicable, as follows





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[1] This article is based upon a thesis submitted by Victor C. Rogers to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] DuPont Fellow in Chemistry.

[3] Pfeiffer, "Organische Molekülverbindungen," F. Enke, Stuttgart, 1922, p. 250.

[4] Schmidlin, "Das Triphenylmethyl," F. Enke, Stuttgart, 1914, p. 75.

[5] (a) Gomberg, *Ber.*, 34,2730 (1901); (b) 38,2449 (1905).

However, the later discovery of addition products of hexaphenylethane with both olefin and saturated hydrocarbons,[6] in which the nature of the binding cannot be so explained, has led to some hesitation in suggesting structures for these complexes.

The alkyl sulfides are known to form a great number of complexes with both organic[7,8] and inorganic compounds.[9] The nature of some of these complexes has been interpreted by the use of the sulfonium theory, analogously to the conception of the oxygen linked complexes. One might expect then that hexaphenylethane with its remarkable additive tendency would form complexes with the alkyl sulfides. No mention of the formation of these substances is to be found in the literature, except for the statement by Schmidlin[10] that they have not been prepared. The preparation and a study of the properties of the methyl, ethyl and propyl sulfide addition products have been undertaken. The details of the preparation are found in the experimental part.

Properties of the Crystalline Addition Compounds

The crystals are colorless to light yellow in color. They are easily soluble in such solvents as benzene, ether, chloroform and the organic sulfides. The solutions are very sensitive to the action of the oxygen of the air; on standing in open vessels or when air or oxygen is passed through the solutions, the characteristic white peroxide is precipitated.'

We expected to find the sulfide addition compounds to be much more stable or inert than the analogous compounds involving oxygen linkage. Such is not the case. The strength of the bond between the sulfide and the hexaphenylethane appears to be of the same order as that in the complexes with ethers and esters. The sulfide is partially lost by washing the crystals with solvents of various kinds. The crystals also give up the alkyl sulfide when placed in a slow stream of carbon dioxide. This occurs to some extent even at room temperatures; a sample standing overnight lost about 20% of its sulfur content.

In the formation of the addition compounds of hexaphenylethane with esters, ketones, carbon disulfide, etc., Gomberg and Cone[11] found that although in general the ratio of the added substance to hexaphenylethane was one mole to one mole, varying results were obtained depending upon the temperature of preparation, nature of the solvent used to wash the crystals of the addition product and the amount of washing done. In the case of the ethyl sulfide addition product we obtained a consistently

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[6] Gomberg and Schoepfle, THIS JOURNAL, 37,2569 (1915).

[7] Oefele, Ann., 132, 82 (1864).

[8] Cahours, Ann., 135, 352 (1865).

[9] Ref.3, p. 125.

[10] Ref. 4, p. 81.

[11] Gomberg and Cone, *Ber.*, 38, 1333, 2447,2451 (1905).

good ratio. With the methyl sulfide addition product greater irregularities of composition were encountered. However, there is no doubt that the figures (see experimental part) are of the magnitude demanded by the 1:1 ratio of the hexaphenylethane to the methyl sulfide. No satisfactory results were obtained with the crystals separating from the propyl sulfide. In this case careful drying resulted in a very low sulfur content, while less rigid drying gave a percentage somewhat above the theoretical value. It is interesting to note that the dipropyl ether compound with hexaphenylethane which Gomberg and Cone[12] prepared also gave no constant figure for the ether content.

Oxidation of the Alkyl Sulfide Addition Products

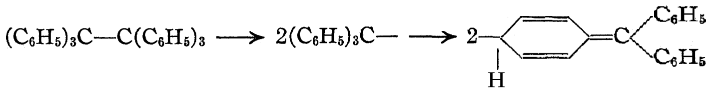
The absorption of oxygen by solutions of hexaphenylethane and related compounds has been shown by Gomberg and his co-workers[13] to be of the magnitude to warrant the equation

$$(C_6H_5)_3C\text{—}C(C_6H_5)_3 + O_2 \longrightarrow (C_6H_5)_3C\text{—}O\text{—}O\text{—}C(C_6H_5)_3$$

However, the reaction is clearly influenced by outside factors, for the yield of the triphenylmethyl peroxide may vary considerably according to the solvent used,[14] and also depending upon whether pure oxygen or air is used as the oxidizing agent.[15]

Now Moureu and Dufraisse[16] have pointed out the activity of sulfides, including the alkyl sulfides, in altering the rate of oxidation of auto-oxidizable substances, while Taylor[17] has pointed out the connection between catalysis of auto-oxidation and the property of addition complex formation.

It had been observed during the course of the work that the yellow color of the solutions of hexaphenylethane in pure alkyl sulfides was considerably deeper than when benzene or ether was used as the solvent. If the color is due to quinoxidation as proposed by Gomberg,[18] and Jacobson,[19] it would seem that the alkyl sulfides possess the property of shifting the equilibrium markedly toward the quinoid tautomer.



A test of this hypothesis could be made by studying the oxidation of hexaphenylethane in alkyl sulfide solutions, because it has been established

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[12] Gomberg and Cone, *Ber.*, 38, 2449 (1905).

[13] Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, 1924, p. 88.

[14] Gomberg and Sullivan, THIS JOURNAL, 44, 1817 (1922).

[15] Gomberg and Cone, *Ber.*, 37, 3538 (1904).

[16] Moureu and Dufraisse, *Compt. rend.*, 178, 1861 (1924).

[17] Taylor, *J. Phys. Chem.*, 27, 322 (1923).

[18] (a) Gomberg, *Am. Chem. J.*, 25, 334 (1901); (b) *Ber.*, 1824 (1902).

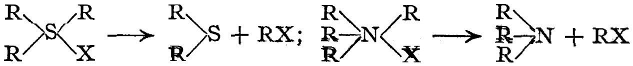
[19] Jacobson, *Ber.*, 38, 196 (1905).

that the colored modification is rapidly transformed by air or oxygen into triphenylmethyl peroxide.[20]

Experiments were carried out to measure the rate of oxidation of hexaphenylethane in the presence of alkyl sulfides and also in the presence of other additive substances. The results as pictured by the curve in the experimental part show clearly that the presence of the alkyl sulfides has a marked accelerating effect. This may be explained by assuming that the sulfide increases the concentration of the quinoid or easily oxidized tautomer. Total absorption measurements showed this to be unaffected by the presence of the sulfides.

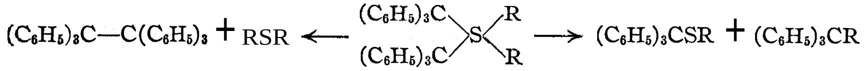
Thermal Decomposition of the Alkyl Sulfide Addition Products

When the alkyl sulfonium compounds and the quaternary ammonium compounds are heated, the following type of splitting occurs



$$\begin{matrix}R\\R\end{matrix}\!>\!S\!<\!\begin{matrix}R\\X\end{matrix} \longrightarrow \begin{matrix}R\\R\end{matrix}\!>\!S + RX;\quad \begin{matrix}R\\R\\R\end{matrix}\!\!\rightarrow\!N\!<\!\begin{matrix}R\\X\end{matrix} \longrightarrow \begin{matrix}R\\R\\R\end{matrix}\!\!\rightarrow\!N + RX$$

If the hexaphenylethane-alkyl sulfide complexes possess the sulfonium structure, an analogous splitting should occur and probably in two ways, as follows



$$(C_6H_5)_3C{-}C(C_6H_5)_3 + RSR \longleftarrow \begin{matrix}(C_6H_5)_3C\\(C_6H_5)_3C\end{matrix}\!>\!S\!<\!\begin{matrix}R\\R\end{matrix} \longrightarrow (C_6H_5)_3CSR + (C_6H_5)_3CR$$

so that we should find among the decomposition products mixed sulfides containing the triphenylmethyl group, and hydrocarbons of the a, a, α-triphenyl paraffin type.

It has been noticed that when the addition compounds of hexaphenylethane are warmed, they lose to a greater or less extent the added substance. In some cases this loss is nearly quantitative, but in other cases the result is below that corresponding to the one mole to one mole addition ratio. Furthermore, it has been observed frequently that the material left after driving off the added substance had not entirely the properties of hexaphenylethane. In the case of the sulfide additions, a positive test for sulfur in the residue indicated a decomposition in addition to the simple dissociation of the addition compound.

Attempts were made to retard the dissociation by heating in sealed tubes. Although complex, the resulting mixture could be separated into two classes—complex hydrocarbons of low volatility, probably of the α, a, a,-triphenyl paraffin type, and compounds containing sulfur and triphenylmethyl groups, also of low volatility. These results are explained most simply by the assumption of a sulfonium structure for the addition compound and a splitting in such a way that the two triphenylmethyl groups are separated to take part in the formation of two new molecules

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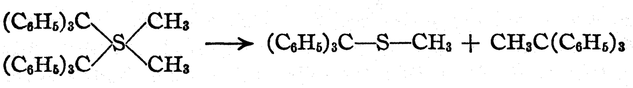
[20] **Schmidlin, *Ber.*, 41, 2476** (1908).



$$[(C_6H_5)_3C]_2S(CH_3)_2 \longrightarrow (C_6H_5)_3C{-}S{-}CH_3 + CH_3C(C_6H_5)_3$$

Experimental Part

Preparation of the Addition Compounds.--The hexaphenylethane was prepared by treatment of a solution of triphenylmethyl chloride with mercury.[21] It was found most convenient to prepare the addition compounds by using the respective sulfides as the solvent in which to prepare the hexaphenylethane. The preparation was carried out in a large deformed "U"-tube. The limbs of the "U" were sealed and near the bend was affixed a small side arm. Through this arm the reactants were introduced into the far limb of the vessel. Two and seven-tenths g. of triphenylmethyl chloride, 1.7 cc. of mercury and 8–10 cc. of carefully dried alkyl sulfide were used in each preparation. The vessel was then evacuated until quiet boiling of the solvent displaced most of the air present. The side arm was then sealed and the vessel agitated in such a manner that the mixture was always confined to one arm of the "U."

After agitating for two or three days the vessel was supported vertically and the mixture allowed to settle, after which the clear, deep yellow solution of hexaphenylethane was decanted carefully into the opposite arm of the "U." By warming the limb containing the solution and cooling the other most of the solvent was distilled away from the hexaphenylethane. Upon standing, colorless or pale yellow crystals separated. After crystallization the mother liquor was decanted back into the opposite limb and then by cooling the limb containing the crystals pure solvent was condensed upon the crystals for washing them. When the crystals were washed sufficiently they were dried by warming them gently or by cooling the opposite limb in a cooling mixture. In this manner the crystals were prepared, washed and dried in an atmosphere free from oxygen. When the operation was completed, the limb of the vessel was circled with *a* file scratch and broken off in an atmosphere of carbon dioxide. The above method yielded from one to two grams of solid product from each preparation.

Analysis.—Qualitative examination of the crystals showed no mercury, a trace of chlorine and a strong test for sulfur.

An attempt was first made to analyze the compounds after the method of Gomberg and Cone[12] by heating them in a stream of carbon dioxide to 60–80° until constant weight was attained. The loss of alkyl sulfide was always below the theoretical amount and the residue gave a test for sulfur, indicating that all of the sulfide was not lost in this way.

Determination of the sulfur content of the crystals was carried out by first heating in a Carius tube at 200° for eight hours with fuming nitric acid and a drop or two of bromine. This was followed by a fusion with a mixture of potassium hydroxide and sodium peroxide. The sulfur was then determined in the usual manner as barium sulfate.

The results were as follows:

Ethyl sulfide-hexaphenylethane: Calcd.: S, 5.56. Found: 5.48, 5.42, 5.43. Methyl sulfide-hexaphenylethane: Calcd.: S, 5.83. Found: 6.02, 5.31, 5.28, 4.98, 4.80, 4.83. Propyl sulfide-hexaphenylethane: Calcd.: S, 5.31. Found: 2.90, 2.78, 2.28, 1.30, 6.56, 6.33, 5.96, 7.37.

Oxidation Rate.—The alkyl sulfide-hexaphenylethane addition product was not isolated in the solid form for these experiments, but a solution resulting from the conversion of *a* definite amount of triphenylmethyl chloride in bromobenzene solution containing an equivalent of the additive substance was used. One-fourth of a gram of triphenylmethyl chloride, 0.5 cc, of mercury and 10 cc. of dry bromobenzene containing about four drops of the sulfide were sealed in an 11cc. thin-walled bulb which had been pre-

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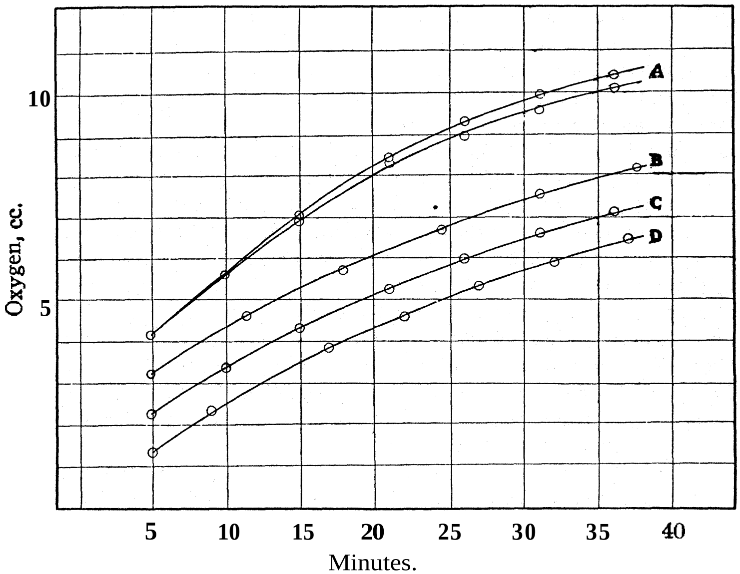
[21] Ref. 4, p. 30.

viously dried and swept out with nitrogen. This bulb was then agitated vigorously for eight hours, at which time all of the triphenylmethyl chloride had been converted to hexaphenylethane as shown by a total absorption. The bulb was then placed in a small vessel equipped with a manometer and a plunger for breaking the bulb. After the introduction of *a* few drops of bromobenzene the vessel was swept out with oxygen, closed and a few moments allowed for the saturation of the confined oxygen with bromobenzene vapor.

After recording the temperature, pressure and the position of the levels of the manometer tubes, the bulb containing the sample was completely crushed by striking the plunger in the vessel. As the oxygen in the vessel was absorbed, atmospheric pressure was maintained by continuous adjustment of the manometer levels. The position of the adjusted levels of the manometer was periodically recorded. The absorptions were carried out at 23.5°.



A, alkyl sulfide; B, acetone; C, carbon disulfide; D, bromobenzene.

Fig. 1.

The curves shown represent about two-thirds of the total absorption **taking** place over about forty minutes of time. The starting point of all of the curves is the same but the curves have **been** moved apart in order to emphasize the similarity of difference of slope. It is apparent from Curves II and III that the rate of oxidation is the same in the case of carbon disulfide and acetone and that it does not differ from the rate **when** bromobenzene alone is used. Curve I, on the other hand, representing the rate of oxidation in the presence of alkyl sulfides, has a much steeper slope than the other three, particularly during the first two-thirds of the reaction time.

Total Absorption.—Samples of hexaphenylethane in bromobenzene and in bromobenzene containing an equivalent amount of ethyl sulfide were prepared in the same manner as those used for the rate absorption measurements. These were placed in a glass-stoppered bottle which was connected to the mercury manometer of the previously used apparatus by means of a heavy-walled rubber tube. The bottle was shaken vigorously for five minutes. With the breaking of the sample tube the mercury rose immediately and at the end of five minutes the sample had absorbed from 11.2 to 11.3 cc. of oxygen, more than 10 cc. of this being absorbed in the first minute. At the end of the first minute the rate was very slow.

For three samples in bromobenzene only the absorption was: (a) 11.2, (b) 11.2, (c) 11.3; theoretical, 11.8. For three samples in bromobenzene containing ethyl sulfide: (a) 11.2, (b) 11.3, (c) 11.3.

Thermal Decomposition of the Addition Product.—A sample of hexaphenylethane dissolved in a large excess of methyl sulfide was heated in a sealed tube at 150° for eight hours. The resulting mixture was still yellow in color. Enough benzene was added to attain solution. Air was passed through the solution in order to convert any unchanged hexaphenylethane to the difficultly soluble peroxide. The small amount of solid resulting was separated by filtration. The filtrate was then evaporated and the solid residue was separated into several parts by fractional crystallization with petroleum ether and alcohol as solvents.

All of these fractions were solids or thick oils. Some contained sulfur and others did not. No attempt was made to carry out ultimate analyses since difficulties of purification and the probable slight variation in the composition of the hydrocarbons of high molecular weight made it extremely doubtful whether information could be obtained in this way. The fractions containing no sulfur showed, however, the general characteristics of hydrocarbons of the triphenyl paraffin class. They were extremely soluble in benzene, petroleum ether, chloroform, carbon tetrachloride, ether and acetone. They were slightly soluble in alcohol and could be recrystallized from this solvent. Concentrated solutions in benzene and petroleum ether showed a strong tendency to supercool and set to a hard, glassy mass without crystallizing. The solids were neither colored nor dissolved by concentrated cold sulfuric acid. Warm acid (80–90°) brought about partial solution and a slight coloring, but dilution of the mixture with water precipitated the substance unchanged.

The sulfur-containing solids were non-volatile and practically odorless; consequently the sulfur could not be present as originally in the molecule of the comparatively low-boiling alkyl sulfide. Attempts to recrystallize some of the sulfur-containing portions resulted in the appearance of the insoluble triphenylmethyl peroxide. This behavior is characteristic of sulfides and disulfides[22] containing triphenylmethyl groups. Also char-

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[22] Blicke, This Journal, 45, 1965 (1923).

acteristic is the ready solubility and yellow to brown coloration in cold sulfuric acid. When the sulfuric acid solutions were warmed, alkyl mercaptans were evolved. The resulting solution when cooled, diluted and made alkaline yielded a solid precipitate which proved to be triphenylcarbinol.

$$(C_6H_5)_3C{-}S{-}R + H_2O\ (H_2SO_4) \longrightarrow (C_6H_5)_3C{-}OH + H{-}S{-}R$$

It seems certain, after consideration of the evidence, that our sulfur-containing products were of the triphenylmethyl alkyl sulfide class.[23]

The authors wish to express their appreciation for the suggestions offered by Professor L. W. Jones during the course of the investigation and also for the aid of the duPont Fellowship held by one of us during the latter part of the work.

Summary

1. Addition products of methyl, ethyl and propyl sulfides with hexaphenylethane have been prepared.
2. It has been found that the alkyl sulfides accelerate the rate of oxidation of hexaphenylethane in bromobenzene solution. This is apparently not so with carefully purified carbon disulfide and acetone, which also yield addition products with hexaphenylethane.
3. Observations have been made concerning the probable course of the thermal decomposition of the hexaphenylethane methyl sulfide addition product.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

CONDENSATION PRODUCTS OF BENZALACETOPHENONE AND SOME OF ITS DERIVATIVES[1]

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Fischer and Knoevenagel[2] found that phenylhydrazine and acrolein react to give 1-phenylpyrazoline instead of the expected hydrazone. Much later Auwers and Müller[3] argued that this product is formed through the rearrangement of an unstable hydrazone, and noted that in those

$$\begin{array}{c} C_6H_5{-}NH{-}{-}{-}N \\ \| \\ H_2C{=}CH{-}C{-}H \end{array} \longrightarrow \begin{array}{c} C_6H_5{-}N{-}{-}{-}N \\ |\qquad\quad \| \\ H_2C{-}CH_2{-}C{-}H \end{array}$$

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[23] Ref. 4, p. 124.

[1] From a portion of the 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 H. L. Davis, August, 1925.

[2] Fischer and Knoevenagel, *Ann.*, 239, 194 (1887).

[3] Auwers and Müller, *Ber.*, 41, 4230 (1908).

cases where the latter can be isolated, heating with acetic acid causes rearrangement. Auwers and Voss[4] isolated the hydrazones of cinnamic aldehyde and benzalacetone and found that they rearrange to the corresponding pyrazolines at higher temperatures or by heating with acetic acid. They concluded that phenylhydrazones from α,β-unsaturated ketones of the type R—CH=CH—CO—R′ can be isolated only when R is an aryl radical. Their failure to isolate the hydrazone of benzalacetophenone indicates that the stability of these products must be influenced also by the character of the radical R'. Its structure seems more important than its weight. When it is an aryl radical, hydroxyl and alkoxyl substituents favor rearrangement, while the nitro group stabilizes the hydrazone.[5] When halogen is present Straus[6] found that the closing of the pyrazoline ring occurs readily when the substituent is in either ketone or hydrazine residue. When both are substituted the hydrazone is quite stable and requires energetic treatment for rearrangement.

These conclusions are here questioned because the methods of preparation seem to be varied too much to permit a fair comparison of the products. In some cases the conditions were such that a hydrazone of this group might rearrange. In others the record does not include positive identification of the products.

In the present study the conclusion of Auwers and Voss that the "hydrazone of benzalacetophenone is so labile that it cannot be isolated, even at low temperature" was first tested. By conducting the experiment in glacial acetic acid solution at room temperature and also by following as carefully as possible the directions of Auwers and Voss, there was obtained a product that melted at 117–120°.[7] This substance was shown to be a hydrazone by examination of its reduction products,[8] and also by observing its direct rearrangement to 1,3,5-triphenylpyrazoline,[9] m. p. 135–136°.

To test the effect of substituents in the ketone and hydrazine residues, previously studied by Straus, and referred to above, attempts were made to prepare hydrazones containing some of the radicals mentioned by him. It will be shown below that in no instance was such a hydrazone isolated, but that in each of the five cases tested the corresponding pyrazoline was obtained.

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[4] Auwers and Voss, *Ber.*, *42*, 4412 (1909).

[5] Auwers and Lämmerhirt, *Ber.*, 54, 1000 (1921).

[6] Straus, *Ber.*, 51, 1458 (1918).

[7] The failure to give a sharp melting point may mean that a rise in temperature caused rearrangement of part of the material into the pyrazoline.

[8] Tafel, *Ber.*, *22*, 1854 (1889).

[9] Knorr and Laubmann, *Ber.*, 21, 1210 (1888); see also Fromm, Ann., 394, 305 (1913).

Experimental Part

Methyl-3-bromo-4-acetylaminophenyl Ketone.—A solution of 2.6 cc. of bromine in 51.2 cc. of glacial acetic acid was dropped during twenty minutes into a solution of 5.12 g. of the acetylamino derivative in the volume of acid indicated above, to which an equal volume of water had been added,[10] while the whole was constantly shaken. After three and three-fourths hours this was poured with rapid stirring into 500 cc. of cold water containing about 1 g. of sodium bisulfite. Flocculent masses of fine needles separated and were removed. Addition of 100 cc. of concd. ammonia solution to the cold filtrate precipitated additional product; yield, 79%. Crystallization from alcohol gave leaflets; m. p. 138–138.5°.[11]

Anal. Subs., 0.5107, 0.2491: 19.79 cc. of 0.1 N $AgNO_3$, 12.4 cc. of N_2 at 20° and 746.5 mm. Calcd. for $C_{10}H_{10}O_2NBr$: Br, 31.25; N, 5.46. Found: 30.93, 5.63.

When the above-described product was refluxed for a few minutes with four times its weight of 6 *N* hydrochloric acid and the hot solution filtered through "Norit," crystals of the hydrochloride of the amino compound were deposited. These were suspended in water, an equal volume of ether was added and, after shaking, the lower layer made faintly alkaline, and extraction with ether completed. Treatment of the dried extract with hydrogen chloride precipitated nearly colorless needles; m. p. 155–156°.

Anal. Subs., 0.2500: 19.87 cc. of 0.1 N $AgNO_3$. Calcd. for $C_8H_9ONClBr$: halogen, 46.10. Found: 45.85.

Five g. of the above-described acetyl derivative was oxidized with potassium permanganate in the presence of magnesium sulfate, the mixture filtered, the filtrate evaporated to one-fourth its volume and acidified with concentrated hydrochloric acid. Crystals of 3-bromo-4-acetylaminobenzoic acid separated; yield, 83%. Crystallization from alcohol gave nearly colorless, long needles; m. p. 226–229°.

Anal. Subs., 0.5164: 20.08 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_9H_8O_3NBr$: Br. 31.00. Found: 31.06.

The same product was obtained in 70% yield by the oxidation of 3-bromo-4-acetylaminotoluene with potassium permanganate. Crystallization from alcohol gave long, colorless needles; m. p. 225–227°. Identity with the above-described product was proved by mixed melting point and analysis.[12]

Styryl-4-acetylaminophenyl Ketone.'—To a solution of 9.36 g. of methyl-4-acetylaminophenyl ketone in 100 cc. of alcohol there was added 5.84 cc. of benzaldehyde and then 11 cc. of 20% sodium hydroxide solution, with stirring. The mixture became orange colored and in ten minutes began to deposit flocculent masses of fine needles. Within two hours the mixture was nearly solid and after four and one-half hours the crystals were filtered off and washed with cold alcohol. When the filtrate was poured into 600 cc. of water a second portion of the product mixed with some resin sepa-

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[10] Baeyer and Bloem [Ber., 17, 965 (1884)] obtained methyl-2-acetylamino-5-bromophenyl ketone by bromination in glacial or dilute acetic acid. With chloroform or sulfuric acid as solvent, bromine went into the methyl radical. In the present work an acetic acid solution of the 4-acetylamino derivative gave a good yield of methyl substituted product mixed with but small amounts of the nuclear compound.

[11] This product cannot possibly be identical with the isomeric bromo-aceto-acetanilide, m. p. 138°, reported by Knorr [*Ann.*, 236, 79 (1886)] and obtained by the action of bromine on the anilide of acetoacetic acid.

[12] It is of interest to note here that Friedländer, Bruckner and Deutsch, *Ann.*, 388, 30 (1912), found 224" for the melting point of 2-acetylamino-6-bromobenzoic acid. Our product cannot be identical with this.

rated.[13] Filtration of the hot alcoholic solution through "Norit," and cooling the filtrate gave yellow crystals; m. p. 160–161°.[14]

Anal. Subs., 0.5021: 18.77 cc. of 0.1 N HCl. Calcd. for $C_{17}H_{15}O_2N$: N, 5.28. Found: 5.23.

Styryl-3-bromo-4-aminophenyl Ketone.—To a mixture of 10 g. of the acetylaminobromophenyl ketone and 6.8 cc. (20% excess) of benzaldehyde in 100 cc. of alcohol, 10 cc, of 20% sodium hydroxide solution was added. The mixture became yellow immediately and red after standing a short time. After four hours the crystals that had formed were filtered off and the filtrate was treated as indicated above. The yield was nearly quantitative. Crystallization from alcohol gave fine, yellow needles; m. p. 146–147°.

Anal. Subs., 0.6807: 22.51 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{17}H_{14}O_2NBr$ and $C_{15}H_{12}ONBr$: Br, 23.22, 26.45. Found: 26.42.

Acetylation of the above product as directed by Sudborough[15] gave almost a quantitative yield of diacetyl derivative. Crystallization from alcohol gave colorless plates; m. p. 130–131°.

Anal. Subs., 0.6035: 15.77 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{19}H_{16}O_3NBr$: Br, 20.72. Found: 20.87.

Styryl-3,5-dibromo-4-aminophenyl Ketone.—A solution of 2 g. of the required dibromo-amino-acetophenone[16] and 1.25 cc. (1.5 molecular proportions) of benzaldehyde in 175 cc. of alcohol was treated with 5 cc. of 20% sodium hydroxide solution and the mixture allowed to stand for twenty-four hours. After filtration to remove a small amount of flocculent material that had separated, a large amount of material crystallized promptly from the filtrate.[17] After an hour this was collected on a filter and the second filtrate diluted with 4 volumes of water as described above. The combined product was crystallized in cream-colored needles from a mixture of benzene and ligroin (60–70°); m. p. 133–134°.

Anal. Subs., 0.3734: 19.6 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{15}H_{11}ONBr_2$: Br. 41.99. Found: 41.94.

The above-described product was further identified by conversion into a diacetyl

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[13] The total weight of material was more than that required by theory, and since the resin could not be separated alone, the yield of the ketone was not determined.

[14] Giua and Bagiellae, *Gazz. chim. ital.*, 51, II, 120 (1921), reported 154° as the melting point of this product in the crude form and 168° after crystallization. Although their analytical data agree with those required by this condensation product, the fact that they give 164–165° as the melting point of *p*-acetylaminoacetophenone, while the accepted value is 168°, suggests the possibility that the melting point they reported for the condensation product was actually made on the starting material. This explanation of the discrepancy is supported by their misinterpretation of the work of Rupe and Koschitz, Z. *Farben-ind.*, 5, 317 (1906), on the condensation of *p*-acetylaminobenzaldehyde with acetophenone and who reported 179° as the melting point of the product. Giua and Bagiellae objected to this on the erroneous assumption that the product had been obtained by the interaction of benzaldehyde and *p*-acetylaminoacetophenone.

[15] Sudborough, J. *Chem. Soc.*, 79, 533 (1901).

[16] Fuchs, *Monatsh.*, 36, 122 (1915).

[17] This behavior was noted in more than 20 different preparations of this material and seemed to be characteristic.

derivative in 90% yield by Blanksma's[18] method. Crystallization from alcohol gave yellow granules resembling sand; m. p. 173–174°.

Anal. Subs., 0.4209: 18.11 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{19}H_{15}O_3NBr_2$: Br, 34.40. Found: 34.37.

The Hydrazone of Styrylphenyl Ketone.—To a solution of 20 g. of benzalacetophenone in 100 cc. of glacial acetic acid, 9.5 cc. of phenylhydrazine was added gradually with shaking and the mixture allowed to stand. After about an hour[19] long, yellow crystals began to separate and for the next fifteen minutes crystallization was rapid; yield, 78%. Repeated crystallization from alcohol gave needles that melted at 117–120°.[20]

Anal. Subs., 0.2923: 19.52 cc. of 0.1 N HCl. Calcd. for $C_{21}H_{18}N_2$: N, 9.39. Found: 9.35.

Rearrangement to the Pyrazoline.[21]—Five g. of the hydrazone suspended in 25 cc. of glacial acetic was gently refluxed and the reddish-orange solution that resulted gradually faded to light yellow. After an hour, when the mixture was allowed to cool, it became an almost solid mass of yellow needles that melted at 135–136°.[22] Crystallization from alcohol caused no change; yield, 95%.

Reduction of the Hydrazone.—Ten g. of the hydrazone suspended in a mixture of 150 cc. of alcohol and 15 cc. of glacial acetic acid was reduced by sodium amalgam as directed by Tafel.[8] The resulting solution was poured off from the mercury, evaporated to half its volume, made strongly alkaline and distilled with steam. The distillate was rendered acid to methyl red and extracted with ether. From this extract aniline was isolated and identified as acetanilide. The aqueous residue was acidified with sulfuric acid and evaporated to dryness. The resulting solid was dissolved in water as far as possible, the liquid made alkaline and extracted with ether. From this dry extract gaseous hydrogen chloride precipitated α,γ-diphenyl-α-propylamine hydrochloride.[23] Crystallization from 6 *N* hydrochloric acid gave long, colorless needles; m. p. 195–195.5". It was further identified by the preparation of the picrate and the acid tartrate.[24]

This hydrazone was also obtained when the experiment was carried out as nearly as could be judged as directed by Auwers and Voss. Five g. of benzalacetophenone was dissolved in 40 cc. of alcohol; 2.38 cc. each of glacial acetic acid and phenylhydrazine were added and the mixture was allowed to stand at room temperature. After twenty-four hours an orange-colored oil had separated which crystallized in twenty-seven days. Filtration gave 2.3 g. of solid that, after recrystallization from alcohol, melted at 117–120°. This product was shown by mixed melting point to be identical with the hydrazone described above. Heating with acetic acid rearranged it to the pyrazoline; m. p. 135–136°.

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[18] Blanksma, *Chem. Weekblad,* 6, 719 (1909).

[19] In this preparation it is necessary to remove the crystals within three hours after they begin to separate or they will be contaminated with the pyrazoline. The filtrate obtained at this point deposited a mixture of the hydrazone and pyrazoline.

[20] The failure to show a constant melting point suggests rearrangement as the heating proceeds.

[21] Though the pyrazoline had no noticeable effect on the skin, the hydrazone of benzalacetophenone exhibited severe vesicant action, producing chemical dermatitis.

[22] Knorr and Laubmann, ref. 9, found 134–135°.

[23] Excess of gas should be avoided since this appears to cause the hydrochloride of the amine to dissolve.

[24] Henrich, *Ann.,* 351, 180 (1907).

1,3-Diphenyl-5-(4-chlorophenyl)-pyrazoline.—To a solution of 20 g. of 4-chlorobenzalacetophenone[25] in 200 cc. of glacial acetic acid the theoretical amount of phenylhydrazine was added and the mixture allowed to stand for four days. The color darkened but no solid was deposited. The liquid was cooled until a part of the acid solidified, the mixture poured into a Büchner funnel and the acid allowed to melt and pass through the filter paper. No solid remained. Upon standing for an hour this filtrate deposited orange-colored needles; yield, 28% in eight hours. Crystallization from alcohol gave diamond-shaped plates; m. p. 129–130°.

Anal. Subs., 0.3587: 10.65 cc. of 0.1 *N* $AgNO_3$. Calcd. for $C_{21}H_{17}N_2Cl$: Cl, 10.67. Found: 10.54.

When 1.5 g. of the above-described material was boiled for one hour with 5 cc. of glacial acetic acid and the solution cooled, no crystals separated. Seeding caused deposition of 1.25 g. of unchanged starting material.

1,5-Diphenyl-3-(4-acetylaminophenyl)-pyrazoline.—Six cc. (20% excess) of phenylhydrazine was mixed gradually with a solution of 13.6 g. of styryl-4-acetylaminophenyl ketone in 75 cc. of glacial acetic acid and the mixture allowed to stand at room temperature for twenty-four hours. A reddish color was developed but no crystals were deposited. When the mixture was poured with stirring into 600 cc. of ice water, a yellow solid separated in nearly quantitative yield. Crystallization from alcohol gave fine, branched, hair-like, yellow needles; m. p. 241–242°. Separate portions boiled with acetic acid and treated with sodium amalgam, respectively, suffered no change.

Anal. Subs., 0.2323: 19.48 cc. of 0.1 N HCl. Calcd. for $C_{23}H_{21}ON_3$: N, 11.83. Found: 11.74.

1,5-Diphenyl-3-(3-bromo-4-aminophenyl)-pyrazoline.—Slightly more than the theoretical amount of phenylhydrazine was gradually added with shaking to a solution of 7.77 g. of the required ketone dissolved in 50 cc. of glacial acetic acid. After one and three-fourth hours "burrs" of crystals appeared on the surface of the liquid. During the next four hours 4.5 g. of orange-colored crystals deposited and were removed. On standing overnight, the filtrate deposited 2.6 g. more of the same material. Crystallization from alcohol gave cream-colored needles; m. p. 200.5°. The product was not affected by boiling acetic acid or by sodium amalgam.

Anal. Subs., 0.5221: 13.35 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{21}H_{18}N_3Br$: Br. 20.40. Found: 20.43.

1,5-Diphenyl-3-(3,5-dibromo-4-aminophenyl)-pyrazoline.—Ten g. of the required ketone dissolved in 25 cc. of acetic acid was treated with 2.8 cc. of phenylhydrazine and the mixture allowed to stand at room temperature. After two days 6.17 g. of orange-colored solid had separated. After removal of this the filtrate deposited more on standing; yield, 72%. Crystallization from alcohol or benzene gave orange needles; m. p. 180–181°. The product could be neither rearranged nor reduced.

Anal. Subs., 0.1716: 7.34 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{21}H_{17}N_3Br_2$: Br, 33.97. Found: 34.37.

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[25] Obtained in 85% yield from Eastman's *p*-chlorobenzaldehyde by Walther and Raetze's method [*J. prakt. Chem.*, 65, 280 (1902)). The rate of this condensation was very rapid. Under the conditions, the action of unsubstituted benzaldehyde on acetophenone required two to three hours with efficient stirring; the p-chloro derivative condensed within one minute. The previous authors reported 103–104° as the melting point of the product, while 113–114° was found in this work. The purity of the material here in question was checked by analysis.

Anal. Subs., 0.4515: 18.55 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{15}H_{11}OCl$: Cl, 14.62. Found: 14.57.

1-(*p*-Bromophenyl)-3-phenyl-5-(p-chlorophenyl)-pyrazoline.—The theoretical amount of 4-bromophenylhydrazine in acetic acid was added to a warm solution of *p*-chlorobenzylidene-acetophenone. The crystals that separated during the first few hours turned out to be *p*-bromophenylhydrazine. The filtrate, which was nearly black by reflected light, gave a 31% yield of pyrazoline on standing for twenty-four hours longer. Fine, cream-colored crystals were obtained by crystallization from alcohol; m. p. 142–143°. The product was not affected by boiling acetic acid or by sodium amalgam, which indicated that it was not a hydrazone.

Anal. Subs., 0.4104: 19.85 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{21}H_{16}N_2ClBr$: halogen, 28.06. Found: 27.90.

Summary

1. A method has been described for the preparation of methyl-3-bromo-4-acetylaminophenylketone and its structure has been established.
2. A condensation product from phenylhydrazine and benzalacetophenone different from that reported by Auwers and Voss has been obtained. Its behavior toward sodium amalgam and its rearrangement when heated with acetic acid show that it is a hydrazone.
3. A number of new halogen substitution products of 1,3,5-triphenylpyrazoline have been obtained. In the preparation of these compounds we have been unable, thus far, to confirm Straus' conclusion that the presence of halogen substituents in all three of the phenyl radicals of the hydrazone of benzalacetophenone stabilizes the compound. Further study is in progress in which it is hoped to test the effect of molecular symmetry of the ketone in this rearrangement.

IOWA CITY, IOWA

[CONTRIBUTION PROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE EFFECT OF CERTAIN BETA SUBSTITUENTS IN THE ALCOHOL UPON AFFINITY AND REACTIVITY IN ACETAL FORMATION

BY JOHN N. STREET AND HOMER ADKINS

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The study of the relations of the structure of the alcohol and aldehyde to the affinity and reactivity manifested in acetal formation has been continued by determining the location of the equilibrium point of the reaction of acetaldehyde with various alcohols which may be regarded as β substitution products of ethanol. The type reaction may be represented as follows

$$CH_3CHO + 2RCH_2CH_2OH \rightleftharpoons CH_3CH(OCH_2CH_2R)_2 + H_2O$$

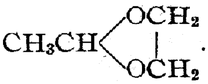
The β substituents used were the chloro, bromo, iodo, ethoxy, methoxy, methylene, carbethoxy, amine hydrochloride and nitro groups.

The methods of experimentation and the concentrations of reactants were essentially the same as those previously described.[1,2] The equilibrium points were determined from both sides in the case of the three halohydrins, phenylethanol and methoxy- and ethoxy-ethanols.

The Seyewetz-Bardin sulfite method was in most cases used for the determination of acetaldehyde. The hydrogen peroxide method was used in some instances. It was necessary to introduce a correction factor in the case of the halohydrins which hydrolyzed slowly during the titration.

In the case of amino-ethanol, acetal formation cannot **take** place in the usual way as the amino group reacts with the aldehyde. The acetal reaction must consequently be carried out with a salt of the amine. The hydrochloride is insoluble in most organic solvents so that the reaction must be allowed to occur in a water solution. The solution of the amine in water was made slightly acid with hydrogen chloride, the aldehyde added at 0° and the reaction allowed to proceed at room temperatures for a week. A sample of the reaction mixture was rendered just alkaline to phenolphthalein and then added to a sulfite solution and titrated in the usual way. The end-point is not clear. The hydrogen peroxide method was also used for the determination of the aldehyde. The results obtained were in good agreement with those obtained by the sulfite method. The reaction of ethanol and acetaldehyde was run under conditions similar to those used for amino-ethanol. The equilibrium constant found was 0.0618 instead of 0.0744 as found using 1 mole of alcohol and 0.091 mole of aldehyde.

An attempt was made to prepare β,β′-hydroxydiethylacetal, $CH_3CH(OCH_2CH_2OH)_2$, by the reaction of acetaldehyde and ethylene glycol. However, even when two moles of the glycol were used with one mole of acetaldehyde, there was a good yield of ethylene acetal



$$CH_3CH\left\langle\begin{array}{l}OCH_2\\ \;|\\ OCH_2\end{array}\right..$$

Attempts to use the sulfite, the hydrogen peroxide and the Hartung colorimetric method were alike unsuccessful in determining acetaldehyde or water in the presence of nitro-ethanol. The amount of acetal that could be isolated from a reaction mixture of two moles of nitro-ethanol and one of acetaldehyde was determined and the equilibrium constant calculated from this. A mixture of 1 mole of nitro-ethanol and 0.091 mole of acetaldehyde was made and allowed to stand for two weeks. A sample of the reaction mixture was poured into a solution of sodium ethoxide to prevent further acetal formation or hydrolysis. The aldehyde present was then removed by distillation, collected and titrated. An equilibrium constant was calculated on the basis of the amount found. This value (0.0403) was too high because it was impracticable to collect all-of

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[1] **Adkins and Adams, THIS JOURNAL, 47, 1368 (1925).**

[2] **Hartung and Adkins, *ibid.*, 49, 2517 (1927).**

the aldehyde. The value calculated from the amount of nitro-ethyl acetal isolated (0.0119) was too low because of losses of the acetal. The true value lies between these limits.

The methods used in the preparation of the reagents and their boiling points are given in Table I and the footnotes. Five acetals not hitherto prepared were obtained using the standard methods of preparation. The boiling points and the analytical data for these compounds are given in Table II.

TABLE I

THE METHODS OF PREPARATION AND PURITY OF REAGENTS

Compound	Boiling point
Ethylene chlorohydrin[n]	43° (3–4 mm.)
Ethylene bromohydrin[b]	56–57° (20 mm.)
Ethylene iodohydrin[c]	86–87' (25 mm.)
β-Ethoxy-ethanol[d]	134' (740 mm.)
β-Methoxy-ethanol[d]	124° (740 mm.)
β-Phenylethanol[e]	99–100° (10 mm.)
Ethyl hydracrylate[f]	94–95° (22 mm.)
β-Amino-ethanol	121° (740 mm.)
β-Nitro-ethanol[g]	......
Propanol	96.0–96.1° (740 mm.)
Acetaldehyde[h]	21–22' (740 mm.)

[a] Commercial ethylene chlorohydrin was dried for several days over anhydrous potassium carbonate and distilled under a pressure of 3-4 mm. at 43°. The samples used for reaction with aldehyde gave no precipitate with a 10% solution of silver nitrate, no color with copper sulfate and only a trace of acidity.

[b] Read and Williams, *J. Chem. Soc.*, **111, 240 (1917)**; Read and Hook, *ibid.*, **117, 121 (1920).**

[c] Henry, *Bull. acad.* roy. *Belg.*, [3] *28*, **182 (1889)**; Wieland and Sakellarios, *Ber.*, **53B, 201 (1920).** It was found advantageous to cut the time of refluxing from 24 to 4 hours, a yield of 85–90% being obtained.

[d] Cretcher and Pittenger, THIS JOURNAL, **46,1505 (1924).**

[e] β-Phenylethanol from a commercial source was kept over solid oxalic acid for several days and then distilled. Later it was dried over lime and again distilled.

[f] Drushel and Holden, *Am. J. Sci.*, **40, 511 (1915).** Drushel and Holden report that the ester prepared from β-iodopropionic acid has a b. p. at 22 mm. of 95.5". The hydracrylic acid was prepared by the hydrolysis of ethylene cyanohydrin. [Erlenmeyer, *Ann.*, **191,268 (1878).**] After filtering off the ammonium chloride, the solution was neutralized with sodium hydroxide, evaporated to dryness and the sodium hydracrylate extracted with absolute alcohol. The salt was recrystallized once from alcohol, dissolved in alcohol and enough of an alcoholic solution of hydrogen chloride added to precipitate 90% of the sodium. The esterification was then carried out using copper sulfate (free of sulfur trioxide) as a catalyst.

[g] Wieland and Sakellarios, Ber., **53B, 201 (1920).**

[h] Child and Adkins, THIS JOURNAL, **45,3013 (1923).**

A summary of the equilibrium constants and calculated values for $-RT \ln K$ is given in Table III. The compounds have been arranged in order of decreasing affinity as measured by decreasing equilibrium con-

TABLE II

BOILING POINTS AND ANALYTICAL DATA FOR CERTAIN ACETALS

Acetal of	B. p.	Analyses Calcd., %	Analyses Found, %
Ethylene chlorohydrin	109–110° (30 mm.)	C137.93	37.95
Ethylene bromohydrin	129–130" (20 mm.)	Br 57.92	58.07
β-Methoxy-ethanol	100° (20–30 mm.)	C 53.84 H 10.18	53.80 10.03
β-Ethoxy-ethanol	83–85° (10–15 mm.)	C 58.20 H 10.75	58.06 10.78
β-Phenylethanol	201° (15 mm.)	C 79.94 H 8.20	80.16 8.27

TABLE III

THE EFFECT OF CERTAIN SUBSTITUENTS IN THE ALCOHOL UPON AFFINITY IN ACETAL FORMATION

Alcohol	β Subs.	Vol., cc.	Conv. to acetal, %	K	− RTln K
8-Amino-ethanol	$HCl\cdot NH_2$	...	[a]	0.235	960 ± 100
n-Butanol	C_2H_5	97.1	95.8[b]	.1850	994 ± 50
Phenylethanol	C_6H_5	124.2	87.55[b]	.0978	1372 ± 50
Ethylene iodohydrin	I	83.3	90.50[b]	.0953	1387 ± 50
β-Ethoxy-ethanol	C_2H_5O	101.8	88.92[b]	.0939	1396 ± 50
n-Propanol	CH_3	79.7	90.50[b]	.0902	1420 ± 50
β-Methoxy-ethanol	CH_3O	83.9	88.63[b]	.0754	1525 ± 50
Ethanol	H	63.0	90.94[b]	.0744	1540 ± 50
Allyl alcohol	CH_2	72.9	88.1[b]	.0616	1653 ± 50
Ethylene bromohydrin	Br	76.2	87.60[b]	.0605	1655 ± 50
Ethylene chlorohydrin	Cl	72.0	86.26[b]	.0453	1826 ± 50
Ethyl hydracrylate	$C_2H_5O_2C$	62.2	66.2[b]	.0171	2400 ± 50
8-Nitro-ethanol	NO_2	77.5	83.3[b]	(.0403)	1895
		...	...[c]	(.0119)	2600

[a] 0.335 mole of amino-ethanol, 1.242 moles of water and 0.0955 mole of aldehyde showed 21.8% conversion to acetal in a volume of 54.25 cc.

[b] One mole of the alcohol and 0.091 mole of acetaldehyde showed the per cent. conversion indicated, in the volume given in the preceding column. The per cent. conversion given in the table is the average of from four to seven determinations, including in most cases synthetic and hydrolytic experiments. The individual determinations were within 0.5% of the average.

[c] 0.0505 mole of the acetal was isolated from 0.288 mole of nitro-ethanol and 0.273 mole of acetaldehyde.

stants and increasing values for —RT ln K. There have been included in the table for the sake of comparison the redetermined values for butanol, propanol, ethanol and phenylethanol. (The authors are indebted to Mr. A. E. Broderick for the values for butanol and ethanol.) It is believed that the values of —RT ln K given in the table are accurate to within plus or minus 50 units for all except the first and last alcohols given. Since it was necessary to treat the hydrochloride of β-amino-ethanol with acetaldehyde in a water solution the conditions of this reaction are not directly comparable with the others given in the table. The values given for P-nitro-ethanol are, at best, approximations.

Certain relations become obvious from a consideration of the values given in the table and a comparison of them with previously published values. The order of the halogens, when substituted in the beta position in ethanol, in decreasing affinity for the acetal reaction is the usual one of iodine, bromine and chlorine. However, iodine is more "positive" than is hydrogen in this case for the value of $-RT \ln K$ is 153 units less than for the unsubstituted ethanol. However, ethylene bromohydrin shows a decrease in affinity as compared with ethanol. Hartung showed that the substitution of bromine in acetaldehyde increased affinity for the acetal reaction. The substitution of ethyl, phenyl or methyl groups in the beta position in ethanol increases affinity for acetal formation. The ethoxy group increases affinity by 144 units while the methoxy group has little or no effect.

Hartung showed that the substitution of the methylene group in acetaldehyde (acrolein) decreased the affinity by about 1700 units. In contrast with this is the fact that the substitution of the methylene group in the alcohol (allyl alcohol) has relatively little effect, only lowering affinity by about 100 units.

The carbethoxy group is quite effective in decreasing affinity, the substitution of this group for a beta hydrogen in ethanol lowering affinity by 860 units.

In general it may be said that substitution in the beta position of ethanol has relatively little effect upon affinity for acetal formation. The effect is only a small fraction of what it would be if the substitution were made on the alpha carbon atom and is in the opposite direction in some cases, as, for example, in the case of phenyl and methyl substitution.

It was not possible to obtain any quantitative data upon the relative reactivities of the alcohols studied. In the case of the halohydrins and the ethyl hydracrylate the amount of catalyst present is modified by the small amount of hydrolysis that takes place. The purest samples of the halohydrins obtainable contain, or soon acquire, a concentration of halogen acid which is several times the very small amounts necessary to catalyze the acetal reaction. The methoxy-ethanol and ethylene chlorohydrin showed about 40% reaction of the acetaldehyde in thirty minutes while the n-propyl and phenylethyl alcohols showed a little less than 30% in the same interval. The reactions went from 85 to 90% to completion after several hours. Ethoxy-ethanol was a little slower, while allyl alcohol showed less than 20% reaction in the first thirty minutes. This is rather remarkable since the presence of a double bond in the aldehyde greatly increases reactivity. In general it may be said that the compounds whose **rates** were followed showed no great differences such as one would find in comparing acetaldehyde and benzaldehyde, for example. The greatest difference in reactivity was between the allyl alcohol and the others investigated.

summary

The equilibrium points in the reaction of 8-amino-ethanol, β-phenylethanol, ethylene iodohydrin, β-ethoxy-ethanol, β-methoxy-ethanol, allyl alcohol, ethylene bromohydrin, ethylene chlorohydrin, ethyl hydracrylate and 8-nitro-ethanol with acetaldehyde have been determined. Certain relationships have been pointed out as existing between the constitution of an alcohol and the affinity and reactivity that it manifests in acetal formation. Five acetals not hitherto prepared were obtained.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CARTHAGE COLLEGE]

THE IDENTIFICATION OF ALKYL AND ARYL HALIDES

BY E. L. HILL

RECEIVED AUGUST 17, 1927 PUBLISHED JANUARY 5, 1928

A method for the identification of the primary alkyl bromides and iodides[1] was recently described. This method has now been applied

TABLE I

NEW ALKYL AND ARYL MERCURIC HALIDES

Mercuric bromide	M. p., °C. (corr.)	Formula	Analysis Calcd., %C	Found, %C
Sec.-Butyl[2]	39	....	...	...
Cyclohexyl[3]	153	....	...	...
Benzyl[4]	119	....	...	...
[a]Phenyl[5]	276	....	...	...
m-Tolyl[6]	184	....	...	...
n-Nonyl	109	$C_9H_{19}HgBr$	26.50	26.31
n-Lauryl	108	$C_{12}H_{25}HgBr$	32.029	31.90
*Iso*propyl	93.5	C_3H_7HgBr	11.18	11.13
β-Phenylethyl	169	$C_6H_5C_2H_4HgBr$	24.90	24.81
o-Tolyl	168	$CH_3C_6H_4HgBr$	22.64	22.59
[b]*p*-Tolyl	231[7]	$CH_3C_6H_4HgBr$	22.64	22.61

[a] This method is applicable to the corresponding iodide, m. p. 266°, first prepared by Dreher and Otto, Ann., 154, 109 (1870).

[b] The iodide containing this radical melts at 220° (ibid., p. 173).

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[1] Marvel, Gauerke and Hill, THIS JOURNAL, 47, 3009 (1925).

[2] Marvel and Calvary, ibid., 45, 820 (1923).

[3] Grüttner, Ber., 47, 1651–1656 (1914).

[4] Wolff, Ber., 46, 66 (1913).

[5] Hilpert and Grüttner, Ber., 46, 1686 (1913); Dreher and Otto, Ann., 154, 111 (1870), recorded 291°.

[6] Michaelis, Ber., 28, 590 (1895).

[7] Pope and Gibson, *J. Chem. Soc.*, 101, 736 (1912), found 228°.

successfully to certain secondary alkyl and aryl halides. It involves the preparation of the Grignard reagent and its treatment with the corresponding mercuric halide.

Experimental Part

Table I gives the melting points for several compounds of this class that are known, but which have not previously been identified by this method. It includes also the formulas and analytical data for new secondary alkyl and aryl mercuric halides prepared as indicated above.

Summary

The method already described for the identification of primary alkyl bromides and iodides may be applied with success to secondary alkyl and aryl bromides and iodides.

CARTHAGE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

THE ELECTRON-SHARING ABILITY OF ORGANIC RADICALS—GLUCOSE AND OTHER POLY-ALCOHOLS

BY JAMES B. ALLISON WITH R. M. HIXON

RECEIVED AUGUST 20, 1927 PUBLISHED JANUARY 5, 1928

A preceding paper[1] pointed out that the physical properties of the polar groupings RNH_2, RCOOH, RCH_2COOH, RCH_2CH_2COOH and ROH could be expressed as an exponential function of "the electron-sharing ability" of "R." A strict interpretation of these data implies that the electron-sharing ability of the carbon radicals varies from a range more "positive" than hydrogen to a range more "negative" than chlorine, according to the substituents of the carbon under consideration. When the composition of the radicals is considered in the order of their "negativity," it is found that the typical aromatic groupings are intermediate to the most "positive" and most "negative" of the aliphatic radicals. In other words, we may expect to find carbons in "aliphatic" compounds with properties as negative, or even more negative, than those in "aromatic" structures.

In a previous paper[2] attention was called to the negative nature of the third carbon atom in diacetoneglucose on the following evidence.

1. The chlorine in 3-chlorodiacetoneglucose is relatively stable toward alkaline hydrolysis.

2. When diacetoneglucosetoluenesulfonate ester is treated with Grignard's reagent, *p*-tolylphenylsulfone is obtained in analogy with the aromatic sulfonate esters rather than the aliphatic esters.[3]

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[1] Hixon and Johns, THIS JOURNAL, **49, 1786 (1927).**

[2] Allison and Hixon, *ibid.*, **48, 406** (1926).

[3] Gilman, Robinson and Beaber, *ibid.*, **48, 2715 (1926).**

3. When the sulfonate ester of diacetoneglucose is treated with hydrazine, dehydration as well as substitution takes place, which is analogous to the terpene sulfonate reaction.

The physical data presented in the following paper have been assembled in order to substantiate these qualitative observations and to correlate the chemical properties of the carbohydrate carbons with the properties of the more familiar "aliphatic" and "aromatic" carbons. These data indicate that the "electron-sharingability" of the carbons in the aliphatic poly-alcohols is intermediate to that of the alkyl and phenyl radical. This paper also indicates an experimental method of approach for the study of the affinity of particular carbons in complex structures such as glucose.

Acid dissociation constants for the hexoses have been measured by Osaka,[4] Madsen[5], Euler[6] and Michaelis and Rona[7] by the cryoscopic, saponification and electrode methods. These authors all agree in reporting values of a magnitude of $Ka = 10^{-13}$ for fructose, glucose and sucrose. The dissociation constant for ethyl alcohol is less than 10^{-15} and for phenol 10^{-11}. Madsen by means of the van't Hoff equation calculates the heat of neutralization for these three sugars and finds them to be respectively about 50, 35 and 25% that of the strong acids.

While these measurements are indicative of the semi-phenolic, semi-aliphatic nature of the carbohydrates they must be considered with the following two reservations.

(a) Values of the same magnitude have been reported for some of the aliphatic aldehydes and accordingly these values might be assigned to the hexose aldehydic or ketonic group. Such an explanation could not, however, be applied to sucrose.

(b) Since there are a large number of hydroxy groups, these values might be considered as the sum of many weaker dissociations.

The heat of the replacement of hydrogen by sodium in the general reaction

$$\mathrm{ROH} + \mathrm{Na} \longrightarrow \mathrm{RONa} + {}^1/_2\,\mathrm{H_2} + \text{heat}$$

may also be used as a comparative index of the degree of "acidity" of the hydrogen. Since R is the only variable in the reaction, this gradation must be explained as a function of the electron-sharing ability of R. A series of hydroxides is given in Table I in the order of the magnitude of the heat of this reaction, grading from the strong base sodium hydroxide to sulfuric acid. The values for the poly-alcohols have been taken from de Forcrand's[8] work; the other data are either taken directly or calculated from values given in Landolt-Börnstein.

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[4] Osaka, Z. *physik. Chem.*, 35, 673 (1900).

[5] Madsen, *ibid.*, 36, 290 (1901).

[6] Euler, Ber., 39, 344 (1906).

[7] Michaelis and Rona, *Biochem.* Z.. 49, 248 (1913).

[8] De Forcrand, Ann. *chim. phys.*, [6] 30, 56 (1893).

TABLE I

HEAT OF REPLACEMENT OF HYDROGEN BY SODIUM

Sodium hydroxide	**2.0**	**Mannitol, average value**	**34.82**
Aluminum hydroxide	**27.0**	**Erythrite, average value**	**38 14**
Tertiary alcohol, average value	**27.89**	**Glycerol, average value**	**39.99**
Secondary alcohol, average value	**29.75**	**Phenol**	**39.10**
Primary alcohol, average value	**32.00**	**Acetic acid**	**50.17**
Water	**31.87**	**Sulfuric acid**	**68.00**

Attention should be called to the fact that these values indicate that the sugar alcohol groups and other poly-alcohols are almost as negative as phenol itself.

Dissociation Constant of **Glucosamine.**—The values given above cannot be localized for any particular carbon. From the variation in the reactivity of the various halides, it seems probable that there is a marked difference in the affinity of the various carbons in the glucose chain. It should be possible to measure the electron-sharing ability of any of these carbons by replacing the particular hydroxy group by more polar groups such as the amino or carboxy group. The conductivity of the free hydroxy groups is so small (10^{-13}) that it can be ignored for values of strongly polar groups. If trouble is encountered due to the hydroxy groups, they can be easily muzzled by methylation.

Vellinger[9] has reported the value $pK_b = 6.34$ for glucosamine, which gives the value 4.6×10^{-7} for the basic dissociation constant. This value was obtained by potentiometric measurements in connection with a study of the relationship of rotation to acidity of the solution. This value has been confirmed by conductivity measurements in this Laboratory.

Glucosamine was prepared from the hydrochloride salt by the method of Breuer.[10] It was recrystallized several times from methyl alcohol and checked for purity by Dumas nitrogen analysis and by direct titration. The melting point was indefinite, as reported in the literature, depending upon rate of heating. As the amine was repeatedly recrystallized the melting point was raised from 105–110° as reported to 125–130°. Conductivities of three separate preparations are reported in Table II. The value of μ_0 has been obtained by Washburn's[11] method of extrapolation and is an approximation at best.' A comparison of the basic properties of glucosamine with those of ammonia and hydrazine is shown graphically in Fig. I, data for the latter being taken from Bredig.[12]

When this value for the dissociation constant of glucosamine is compared with the list presented in the previous mathematical treatment,' it shows

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[9] Vellinger, *Compt. rend.*, 182, 1625 (1926).

[10] Breuer, *Ber.*, 31, 2194 (1898).

[11] Washburn, THIS JOURNAL, 40, 122 (1918).

[12] Bredig, Z. *physik. Chem.*, 13, 308 (1894).

TABLE II

CONDUCTANCE OF GLUCOSAMINE

Temp., 25°. $\mu_0 = 200$. Average value of dissociation constant $= 6.5 \times 10^{-7}$. Specific conductance of water, 4.5×10^{-6}.

Concn., millimoles	Molecular conductance	Dissoc. const., $K \times 10^{-7}$
48.51	0.92	10.3
24.20	1.01	6.2
12.12	1.28	4.8
6.06	1.65	4.2
3 03	1.97	3 0
1.52	2 62	2.6
45.20	0.89	8.9
22.60	1 27	9.2
11.30	1.56	6.9
5.65	2.17	6.7
2 82	3.10	6 9
1.41	4 44	7 1
20.52	1.2	7 4
10.26	1.6	8.1
5.13	2 2	6 2
2.56	3.06	6.1
1.28	4.3	6.1

that the "electron-sharing ability" of this particular carbon in the glucose chain is almost exactly intermediate to that of the methyl and phenyl radicals, respectively. As in the previous paper mechanical concepts of valence have been intentionally avoided. The conclusions rest on the assumption that, whatever the mechanistic cause of the conductance, the

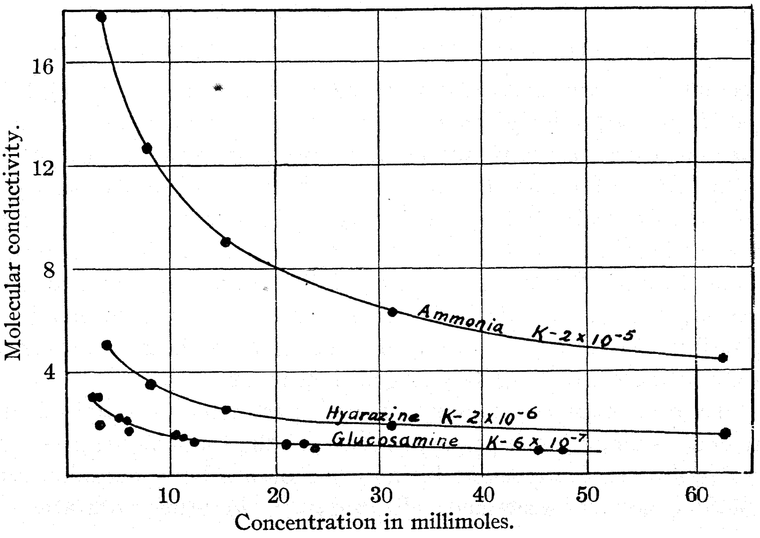

Fig. 1.—Molecular conductivities of ammonia, hydrazine and glucosamine.

magnitude is a function of the "electron-sharing ability" of the radical linked to the amine group.

Summary

It is pointed out that the electron-sharing ability of the aliphatic carbon radicals varies over a range extending from values more positive than hydrogen to values more negative than chlorine. The available physical data have been assembled to show the position of glucose (and other polyalcohols) among the more familiar aliphatic and aromatic radicals. These data agree in showing the intermediate position of this group of compounds as summarized in the following figures.

Nature of radical	Dissoc. const. of amine	Dissoc. of hydroxide	Heat replacement of H by Ma
Methyl-	5×10^{-4}	10^{-15}	32
2-Glucosyl-	6×10^{-7}	10^{-13}	37
Phenyl-	4×10^{-10}	10^{-11}	39

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON THE PREPARATION OF THE HIGHER ACETYLENES. I. (PRELIMINARY PAPER.) DEHALOGENATION OF 1,1-DICHLOROHEPTANE IN THE VAPOR PHASE

BY ARTHUR J. HILL AND FLOYD TYSON

RECEIVED AUGUST 25, 1927 PUBLISHED JANUARY 5, 1928

Acetylenes, more particularly those of the normal, or alpha type, $RC\equiv CH$, are peculiarly reactive and in consequence may be used for the preparation of many interesting and important types of organic compounds. Unfortunately, however, their applicability in synthetic work is rather restricted because of the difficulty of preparing many of the a-acetylenes in quantity and in a state of purity. The usual methods of preparation involve dehalogenation of dihalides, or olefinic monohalides, with solid, aqueous or alcoholic alkalies, alcoholic sodium ethylate, metallic sodium, sodium amide and, in a few cases, soda lime,[1] magnesium,[2] zinc dust and alcohol[3a] and the Grignard Reagent.[3b]

Failure to obtain satisfactory yields, apart from incomplete removal of halogen, is usually due to one, at least, of the following causes, namely, *(a)* molecular rearrangement by aqueous or alcoholic alkaline reagents to diolefins and iso-acetylenes ($RC\equiv CR$); *(b)* ether formation, when alcoholic alkalies are employed; (c) polymerization. The use of sodium

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[1] Peratoner, *Chem. Zentr.*, 1892, II, 737.

[2] Porcher, *Bull. soc. chim.*, [4] 31, 334 (1922).

[3] (a) Lespieau, *Compt. rend.*, 170, 1584 *(1920)*; (b) 171, 111 (1920).

amide[4] in dehalogenation practice constitutes an important advance in the preparation of a-acetylenes. Thus, like sodium, it is stated to effect the isomerization of an *iso-* to an a-acetylene; as a function of this property, a minimum of iso-acetylene is apparently produced when sodium amide is used to dehalogenate a given halide.

Vapor phase dehalogenation of dihalides has apparently received but little attention, except in connection with the preparation of certain 1,3-diolefins used in the preparation of synthetic rubber. The present investigation (the first of the series) has involved a study of the dehalogenation of 1,l-dichloroheptane[5] (I), $CH_3(CH_2)_5CHCl_2$, in the vapor phase. Halides of this type, in consideration of their constitution, should theoretically undergo dehalogenation with the formation of a larger amount of the a-acetylene and a smaller amount of diolefinic and iso-acetylenic isomers than 1,2-dihalides. Moreover, in view of the fact that dry alkalies are stated not to have the rearranging effect[6] of aqueous or alcoholic alkalies, dehalogenation of dichloroheptane in the vapor phase over soda lime should give a reaction product containing a preponderance of the normal acetylene, 1-heptine (11), ($CH_3(CH_2)_4C{\equiv}CH$).

The writers have passed dichloroheptane over soda lime in an electrically heated iron tube (see Fig. 1). Temperatures below 360° were found to be unsatisfactory because dehalogenation was incomplete, whereas above 430° extensive decomposition took place. The yield of normal heptine was never above 30% of the unsaturated compounds constituting the reaction product. The isomerization of α-heptine was apparently affected but slightly by temperature changes between 360 and 420°. At 420° the normal acetylene content of the reaction product was 28% (10% calculated from dichloroheptane), while at 360° the yield was 25% (6% calculated from dichloroheptane). Losses through decomposition and polymerization were also large. The fact that the a-acetylene constituted so small a portion of the unsaturated distillate indicated extensive molecular rearrangement, unless 1-heptine is far more susceptible to polymerization or decomposition than its isomers. Certainly the **P-**acetylene, and other unsaturated compounds derived from the initially formed a-acetylene, were decidedly in predominance in the reaction product.

Variations in the composition of the soda lime did not appreciably affect isomerization. This was decidedly advantageous in view of the fact that soda lime containing 25% of sodium hydroxide was less efficient as a dehalogenating agent than that containing 50% of the alkali. So

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[4] Among others, see Bourguel, Ann. *chim.*, 10, 191,325 (1925).

[5] Dichloroheptane, rather than a lower homolog, was chosen for this preliminary investigation by reason of the accessibility of the corresponding aldehyde and the fact that the derived acetylenes, being oils, were easily handled.

[6] Faworsky, J. *prakt. Chem.*, 37,382,417,531 (1888).

far, then, as rearrangement phenomena are concerned, the vapor phase procedure does not appear to give results very different from those obtained by the employment of alkaline solutions.

A pyrogenetic dehalogenation of the dichloride at 470° over aluminum silicate effected almost complete decomposition and the yield of α-acetylene was very small—less than 2%.

Experimental Part

1,1-Dichloroheptane.—Although dichloroheptane has found fairly extensive use, there is insufficient detailed information regarding its preparation from heptaldehyde[7] and phosphorus pentachloride. In order that large quantities of the dichloride might be employed, and suitable technique developed for the preparation of other similarly constituted dihalides, a number of experiments were carried out to determine conditions most favorable for its preparation.

The chief loss in the preparation of dichloroheptane is due to polymerization of the aldehyde by the acidic reaction mixture. To obviate this effect to some degree, the writers found it necessary to use a solvent and stir rapidly in order to effect immediate dispersion of the aldehyde. The most favorable temperature was 20°; above this temperature the residual material, after distillation, increased very appreciably, and at 65° polymerization had increased to such an extent that the yield was approximately one quarter that obtained at 20°. Amounts of phosphorus pentachloride above or below $1-1^1/_4$ molecular equivalents were not as effective as the latter figures. Some loss is also incurred by the formation of chloroheptene.[8] A serious factor also to be reckoned with is the purity of the phosphorus pentachloride. Erratic and unsatisfactory results, characterized by excessive polymerization, were often obtained when other than fresh samples of phosphorus pentachloride were used. Although the best yield under optimum conditions was 70%, this was not as readily achieved when large quantities of the aldehyde were used.

Apparatus—A wide-mouthed flask equipped with dropping funnel, the stem of which reaches below the surface of the liquid; a thermometer with bulb in the reaction mixture, and a mercury-sealed stirrer capable of rapid rotation.

Procedure.—25 g. of heptaldehyde was added, during forty-five minutes, to a suspension of 45 g. of phosphorus pentachloride in 15 g. of benzene. The temperature was not allowed to rise above 20°. After addition of the aldehyde, the mixture stood at 25° for several hours (it may be allowed to stand overnight). Throughout the experiment the liquid remained light yellow in color. The phosphorus oxychloride was removed by adding ice to the reaction mixture and the dichloride extracted with benzene, washed with sodium carbonate, and dried over sodium sulfate. Distillation at 40 mm.

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[7] The writers are greatly indebted to Dr. Herbert Guest of the J. B. Williams Company, Glastonbury, Conu., who kindly furnished the heptaldehyde used in this investigation.

[8] Cf. Bourguel, *Compt.* rend., 177, 823 (1923).

gave 28 g. of crude dichloroheptane boiling at 75–100° (b. p. 82–84" at 30 mm.). The residue was 11.2 g.

As stated in the introduction, the yields with larger quantities are liable to be lower. The following is a typical run in which 100 g. of heptaldehyde was used, Fraction 3 being practically pure dichloroheptane.

Fraction 1	50–70° (30 mm.)	= 5 g.
Fraction 2	70–80° (30 mm.)	= 5 g.
Fraction 3	80–100° (30 mm.)	= 73 g.
Fraction 4	100–115° (30 mm.)	= 5 g.
Fraction 5	115–140° (30 mm.)	= 11 g.

1-Heptine.—The soda lime used in these experiments was prepared by adding the desired amount of pulverized quicklime to molten sodium hydroxide at 900–1100°. The fused mass, after cooling, was crushed to 6 to 12 mesh.

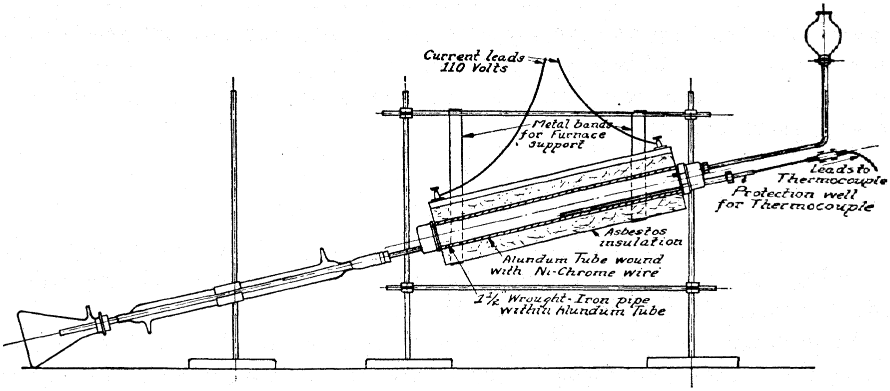

Fig. 1.—Electric furnace for dehalogenation experiments with soda lime.

The reactions were carried out in an electrically heated iron tube which is illustrated above (Fig. 1).

The accompanying chart gives a résumé of some typical experiments with this apparatus. Fresh soda lime was used in each experiment. This precaution appeared necessary for after each run, in which 100 g. or more of dichloroheptane was used, there was an appreciable deposit of carbon.

TABLE I

THE ACTION OF SODA LIME ON DICHLOROHEPTANE

Expt. no.	Dichloroheptane, g.	Soda lime, g.	Temp., °C.	Fraction to 116°, g.	1-Heptine in 116° fraction, %	Yield of 1-heptine calcd. from dichloroheptane, %
1	100	350 (50% NaOH)	360	11.3	30	6
2	150	300 (50% NaOH)	400	31.6	14	5
3	100	300 (50% NaOH)	420	21.0	28	10
4	30	250 (50% NaOH)	430	14.0	7	6
5	100	350 (25% NaOH)	410	13.4	25	6
6	100	300 (Aluminum silicate)	470	8.7	14	2

The conditions represented by Expt. 3 were found in general to be the most favorable. The distillation figures in experiments of this type were usually of the following order:

Fraction 1	80–90°	0.7 g.	Fraction 4	116–150°	4.7 g.
Fraction 2	90–100"	2.3 g.	Fraction 5	150–180°	16.2 g.
Fraction 3	100–116°	18.0 g.	**Residue**	....	3.5 g.

The isomeric heptines, alpha, or 1-heptine, and beta, or 2-heptine, boil at 99–100° and 111–113°, respectively. In consequence, the distillates up to 116° contained the isomeric acetylenes; these were analyzed for 1-heptine as described below. The acetylene distillates were halogen free, or at most contained but a trace of chlorine.

In Expt. 6 the furnace was charged with aluminum silicate in the form of porous cylindrical sticks, $^1/_2''$ long by $^1/_4''$ in diameter. Throughout this run copious fumes of hydrogen chloride issued from the furnace and decomposition was very pronounced. All fractions contained chlorine, hence the analyses were not wholly accurate. The data obtained, however, indicated very small amounts of 1-heptine. A typical distillation is given below:

Fraction 1	Up to 116°	8.7 g.
Fraction 2	116–150°	12.0 g.
Fraction 3	150–200°	9.4 g.

The experiment demonstrated the impracticability of pyrogenetic dehalogenation without the use of some acceptor for the hydrogen chloride resulting from the thermal dissociation.

Procedure for the Determination of **1-Heptine.**—In order to determine the a-acetylene formed in each experiment, two methods of analysis were employed, namely, (a) precipitation with ammoniacal cuprous chloride and (b) precipitation with an alcoholic silver nitrate solution. The former was carried out by agitating the heptine-containing oil with ammoniacal cuprous chloride for six hours. The yellow copper salt was filtered, washed with ether, and dried and weighed as $CuC\equiv C(CH_2)_4CH_3$. The rate of precipitation was slow and greatly affected by the concentration of ammonia. With strong solutions it was decidedly incomplete. The slowness of precipitation of the copper salt and the consequent inaccuracies led the writers to place greater reliance on the silver nitrate method.

Silver Nitrate Procedure.—This method, first introduced by Behal,[9] is based on the insolubility of the salts of the formula $RC\equiv CAg.AgNO_3$, formed in accordance with the following equation

$$CH_3(CH_2)_4C\equiv CH + 2AgNO_3 = CH_3(CH_2)_4C\equiv CAg.AgNO_3 + HNO_3$$

A *5%* solution of silver nitrate in 95% alcohol was used by the writers. A few preliminary experiments showed that a moderate excess of silver nitrate did not affect the analytical results.

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[9] Behal, *Ann. chim. phys.*, [6] 15, 424 (1888).

To carry out an analysis, 0.5 g. of the heptine-containing oil was placed in an excess of the silver nitrate solution. Precipitation of the fine, white crystalline salt took place immediately, but the mixture was usually allowed to stand for six hours before filtration. At this point two procedures were followed. One method was to filter the precipitate upon a weighed Gooch crucible. It was then washed thoroughly with alcohol and dried at 60°. The other procedure consisted in titrating the nitric acid liberated by the formation of the silver salt. In this case the precipitate was first filtered and washed. The united filtrates were then diluted with water to about 300 cc. and the excess silver precipitated by the addition of pure sodium chloride. The nitric acid was then titrated with sodium hydroxide, phenolphthalein being used as an indicator. The titration procedure was utilized in this investigation, since the gravimetric method gave results 2–3% higher than the former method, probably because of adsorption of silver and the retention of moisture. The salt decomposed slowly above 100°, so that thorough drying at atmospheric pressures was impracticable.

Summary

1. Dichloroheptane has been passed over soda lime at various temperatures in an electrically heated tube and the 1-heptine content of the reaction products determined by the silver nitrate method.
2. The yield of 1-heptine was small on account of molecular rearrangement, polymerization reactions and decomposition resulting from the employment of high temperatures necessary to effect dehalogenation.
3. The extent of molecular rearrangement by this method, contrary to previous views on the effect of dry alkalies, is apparently quite comparable to that resulting from the use of alkali solutions.
4. A procedure for the preparation of 1,1-dichloroheptane is described.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE RATE OF SYNTHESIS AND HYDROLYSIS OF CERTAIN ACETALS

BY HOMER ADKINS AND A. E. BRODERICK

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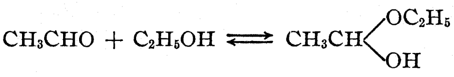
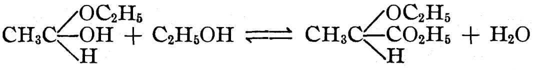
In a previous publication upon the relationship of the structure of alcohols and aldehydes to their reactivity in acetal formation,[1] a comparison of the rates of reaction was made upon the basis of "velocity constants" calculated according to the equation $k = \frac{2.302}{(a_e - b_e)t} \log \frac{(a_e - x)b_e}{(b_e - x)a_e}$, where a, and b_e represented the concentration of alcohol and aldehyde, respectively, at equilibrium and x the change in aldehyde concentration in time, t. As pointed out by the authors,[2] this empirical expression of Muller's has no justification except in the fact that for the first hour of the reaction fairly consistent "constants" are obtained, and that, apparently, by its use one may compare rates of reactions going to very different equilibrium points.

The treatment of the experimental results has been somewhat facilitated by the conclusion from the measurements of the refraction indices and densities of mixtures of certain alcohols and aldehydes,[3] that in some cases one molecule of alcohol reacts immediately with one molecule of aldehyde to form a hemiacetal.



$$CH_3CHO + C_2H_5OH \rightleftharpoons CH_3CH\begin{cases}OC_2H_5\\OH\end{cases}$$

The synthetic reaction whose rate is studied is then that of the hemiacetal with alcohol



$$CH_3C\begin{cases}OC_2H_5\\OH\\H\end{cases} + C_2H_5OH \rightleftharpoons CH_3C\begin{cases}OC_2H_5\\CO_2H_5\\H\end{cases} + H_2O$$

The reaction may then be treated as a bimolecular reversible reaction and the expression $dx/dt = k_1 (a - x)(b - x) - k_2X^2$ applied to the experimental results, where k_1 is the rate of the synthetic reaction, k_2 the rate of the reverse reaction, a and b the initial molar concentrations per liter of alcohol and hemiacetal, respectively, and x is the molar conversion of hemiacetal at time, t. k_1 or k_2 may be expressed in terms of the other and of the equilibrium constant, since $k_1/k_2 = K$, the value of K being calculated from the expression

$$K = \frac{\text{concn. acetal X concn. water}}{\text{concn. alcohol X concn. hemiacetal}}$$

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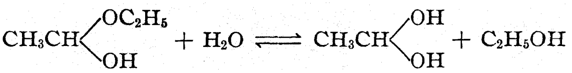
[1] Adkins and Adams, THIS JOURNAL, 47,1368 (1925).

[2] Ref. 1, p. 1378.

[3] Adkins and Broderick, THIS JOURNAL, 50, No. 2 or 3 (1928).

However, there is good reason for suspecting that hemiacetal reacts with water to form aldehydrol as well as with alcohol to give an acetal.



$$CH_3CH\begin{matrix}OC_2H_5\\OH\end{matrix} + H_2O \rightleftharpoons CH_3CH\begin{matrix}OH\\OH\end{matrix} + C_2H_5OH$$

A consideration of the three reactions shows that if the equilibrium point of the last reaction noted is quite far to the right, there will be no material reversal of the acetal reaction during the early stages of synthesis because little water will be present; and that the concentration of the aldehyde at any time, t, will not be $b - x$, but $b - 2x$, for every molecule of acetal formed means one molecule of water formed which would then convert a molecule of hemiacetal into aldehydrol. The concentration of the alcohol will remain constant, because every molecule of alcohol going to acetal will be replaced by a molecule of alcohol resulting from the hydrolysis of hemiacetal. The differential equation then becomes

$$dx = k_1' (a)(b - 2x)$$

or

$$k_1' = \frac{dx}{dt} \cdot \frac{1}{a(b - 2x)}$$

The rates of formation of methyl, ethyl, isopropyl and butyl acetals and the rate of hydrolysis of isopropyl acetal have been very carefully measured, using reagents of high purity, specially designed apparatus and a refined technique for analysis. The percentage of aldehyde (hemiacetal) found was plotted against time and a smooth curve drawn. Tangents were drawn to the curve at 2, 3, 6, 12, 18, 24, 30, 50, 75 and 100 minutes, and from the slopes of these tangents the values of dx/dt were calculated in molar concentration per minute. The values of k_1, k_2 and k_1' were obtained by substituting in the differential equation the values of dx/dt so found, the values of x as analytically determined and of a and b as calculated from the initial concentrations.

The data from which the curves were constructed represented in each case the results of several runs and on the average represented about 20 determinations. Very few of the experimental points were more than 1.0% off the curve representing the average. The concentration at equilibrium was checked after several days, although in general it was reached in from 24 to 36 hours. The values obtained during the first three or four minutes of the reaction are of doubtful reliability.

A summary of the numerical results is given in Table I. After the name of each acetal is given the per cent. conversion at equilibrium and the initial concentration in moles per liter of aldehyde and alcohol (or of acetal, alcohol and water in the hydrolytic reaction). The values of the tangents and the moles of aldehyde reacted are given for intervals from 2 to 100 minutes. The calculated value of k_1 or k_2 and k_1' are then given.

The values for the equilibrium constant, disregarding the formation of any hemiacetal, and the corresponding values of $-RT \ln K$ are as follows

Methyl acetal	$K = 0.1033$	$-RT \ln K = +1340$
Ethyl acetal	$K = .0744$	$-RT \ln K = 1540$
Butyl acetal	$K = .1850$	$-RT \ln K = 994$
*iso*Propyl acetal	$K = .00769$	$-RT \ln K = 2876$

TABLE I

THE RATE OF SYNTHESIS OF METHYL, ETHYL, *iso*PROPYL AND BUTYL ACETALS AND OF THE HYDROLYSIS OF *iso*PROPYL ACETAL[a]

	Methyl acetal 94.7% (2.000 moles of CH_3CHO, 21.886 moles of CH_3OH)									
Time, min.	2	3	6	12	18	24	30	50	75	100
dx/dt	0.0503	0.0443	0.0328	0.0244	0.0174	0.0143	0.0133	0.0087	0.0062	0.0031
Moles react.	.120	.164	.280	.446	.564	.662	.740	.942	1.12	1.21
$k_1 \times 10^4$	13.5	122	9.7	8.1	6.3	5.6	5.6	4.4	3.9	2.2
$k_1' \times 10^4$	14.3	13.3	11.4	11.1	9.9	10.4	12.9			
	Ethyl acetal 90.9% (1.43 moles of CH_3CHO, 15.71 moles of C_2H_5OH)									
dx/dt	0.0405	0.0303	0.0198	0.0123	0.0103	0.0090	0.0070	0.0041	0.0029	0 0023
Moles react.	.114	.144	.224	.314	.379	.436	.486	.600	.665	.743
$k_1 \times 10'$	21.7	18.2	11.8	8.0	7.1	6.8	5.5	4.4	2.9	2.7
$k_1' \times 10^4$	236	18.6	14.1	11.3	10.8	11.2	10.7	12.5		
	*iso*Propyl acetal 59.5% (1.075 moles of CH_3CHO, 12.35 moles of *iso*-C_3H_7OH)									
dx/dt	0.0158	0.0129	0.0085	0.0060	0.0048	0.0043	0.0037	0.0030	0.0020	0.0014
Moles react.	.045	.061	.102	.159	.192	.219	.243	.306	.370	.409
$k_1 \times 10^4$	13.7	11 4	8 0	5.9	5.1	4.9	4.4	4.0	3.3	2.7
$k_1' \times 10^4$	14.3	11.1	8.7	7.2	7.3	6.1	5.7	6.8	5.4	5.0
	Butyl acetal 95.8% (0.851 moles of CH_3CHO, 10.44 moles of C_4H_9OH)									
dx/dt	0.0179	0 0136	0.0087	0 0059	0.0046	0.0034	0.0032	0.0023	0.0014	0.0011
Moles react.	.034	.047	.090	.128	.161	.186	.206	.257	.308	.341
$k_1 \times 10^4$	22.8	17 6	12.1	8.6	7.1	6.5	5.2	4.2	2.8	2.3
$k_1' \times 10^4$	23.8	18.9	10.3	9.1	7.5	7.7	7.1	6.4	6.8	6.7
	*iso*Propyl acetal 40.5% (1.25 moles of acetal, 9.91 moles of *iso*-C_3H_7OH, 1.247 moles of H_2O)									
dx/dt	.....	.....	0.0073	0.0072	0.0068	0.0066	0.0062	0.0042	0.0024	0.0013
Moles react.	.....	.....	.044	.088	.131	.169	.208	.317	,396	.439
$k_2 \times 10^3$	.....	.....	5.2	5.7	6.0	6.6	7.1	7.3	6.7	7.0

[a] The concentration of the catalyst was 0.000465 g. of hydrogen chloride per mole of alcohol in the synthetic reactions and five times that amount in the hydrolysis of isopropyl acetal

The chief point of difference between the experimental results obtained by Adams and those described in this paper is with respect to the faster rate with which methanol reacts with acetaldehytle. However, this does not affect the validity of the conclusion that methanol has a lower reactivity during the initial stages of the reaction than does ethanol. However, it is greater than for butanol and isopropanol.

The method used in this paper for the evaluation of the reaction rates from the experimental results does change the conclusion reached by

Adkins and Adams that *isopropyl* alcohol is more reactive than the primary alcohols. The values of k_1 and k_1' given in the table must lead one to the conclusion that isopropyl alcohol is less reactive than the three primary alcohols studied, although the differences between the four alcohols are not great.

A consideration of the values of k_1 given in the table shows that they rapidly decrease as the synthetic reaction proceeds. The values of k_1' are very much more constant and after the first two or three time intervals are quite constant over a period of from 30 to 60 minutes. The assumption made in the calculation of k_1' is of course justifiable and approximates the truth only in the early stages of the reaction, as it ignores any hydrolysis of acetal and assumes that the active concentration of aldehyde is decreasing twice as fast as the formation of acetal. The limiting point of this assumption is the conversion of 50% of the aldehyde to acetal. The values of k_1' are seen to be constant for a much longer interval in the case of isopropyl acetal than for those acetals which reach an approximately 50% conversion in a shorter time. The values of k_1' lend support to the hypothesis outlined above with regard to aldehydrol formation. The rapid decreases in the values of the constants during the first few minutes are certainly due in a large part to the poisoning effect of water upon the catalyst. The values of k_1' reach a constant value more slowly in the case of isopropyl acetal than with the other acetals. This is understandable because any given concentration of water is reached more slowly in the synthesis of this acetal than with the others; so that the amount of change in k_2 during the period under consideration is relatively small and the value is fairly constant in the period from 24 to 100 minutes. It should be noted that while the values of k_2 for the hydrolytic reaction are roughly ten times those of the synthetic reaction, this is because the concentration of the catalyst is five times as great. With the same concentration of catalyst the rate of the hydrolytic reaction is a small fraction of that for the synthetic reaction. This is further evidence of the poisoning effect of water upon the catalyst.

An inspection of the curves showing percentage conversion of aldehyde against time, even more than an examination of the values given in the table, will lead one to the conclusion that the true reaction rates are individualistic and irregular. For example, if one notes the time required for the reaction to go half-way to equilibrium this is found to be about 50 minutes for methanol, an hour for ethanol and isopropanol, and two or three hours for butanol. Yet the one reaching this point the soonest (methanol) has a lower value k_1' than for ethanol, while butanol requires more than twice as long to reach the half-way point, this too in spite of the fact that the equilibrium points are quite close together. Four and a half minutes are required for 10% of the aldehyde to react with methanol, three minutes for ethanol and about six minutes for the isopropanol and butanol. A comparison of these figures leads to a somewhat different picture of the relative reactivities.

The authors do not believe that the lack of conformity of the experimental curves representing the aldehyde conversion to any precise mathematical pattern is due to impurity of reagents or errors in procedure or analysis. The results have been repeatedly checked by using different sets of reagents under different conditions, using a technique that can be demonstrated to be very accurate.

Experimental

The alcohols were repeatedly dried over fresh lime until the last portion of lime showed no visible crumbling effect at the end of 24 hours' refluxing. (Some ethanol thus dried was refluxed with aluminum ethoxide for 24 hours, but showed no precipitate of aluminum hydroxide. The alcohol so dried was identical in reactivity with that dried over lime only.) The final distillation was performed very carefully, a 46cm. Vigreux column used, the first and last 500 cc. of a 3000cc. lot being discarded and the product protected at all times by guard tubes. The boiling point range was always less than 0.2°.

Acetaldehyde was fractionated from a commercial product through a 46cm. Vigreux condenser surrounded by a water jacket. The vapors before condensation were passed through a 22cm. horizontal column of calcium chloride. Ice water was circulated through the condensers and about the column. All connections were made with paraffined corks. The distillation was discontinued when the temperature of the vapors rose above 21°. The process was repeated three times, the final product being sealed in 5cc. portions in test tubes.

Di-*iso*Propyl Acetal.—In a 2.5 liter bottle were placed 1100 *g*. of *iso*propyl alcohol of commercial grade and 200 g. of specially prepared calcium chloride. The whole was then shaken mechanically for several hours until most of the calcium chloride was dissolved. The mixture was then cooled to near 0° and 425 *g*. of acetaldehyde of commercial grade was added slowly so as to prevent immediate mixing. The bottle was then securely stoppered to resist pressure and the contents were thoroughly shaken. Considerable heat was evolved. The mixture was allowed to stand for twenty-four hours with occasional shaking. At the end of this time no aqueous layer was observed to have formed. The material was filtered through dry potassium carbonate into a flask. It was then distilled under diminished pressure. No very definite fractions could be collected at this time but it was divided into two parts, of which the lower contained most of the alcohol and some aldehyde while the higher was richer in the acetal. The temperature was never allowed to rise above 50°. The average pressure maintained was 25 mm. of mercury. A large quantity of solid material. 200–300 *g*., remained as residue. The two fractions of liquid collected were then fractionated several times. A fraction boiling at 125.5 to 126.5° was collected as di-*iso*propyl acetal. This weighed 251 g. and represented a yield of 18.7%. By making a wider cut the yield could have been increased 3 to 4%, but a less pure product would have been obtained. The pure material was found to have a specific gravity of 0.8128 (25°).

The calcium chloride was prepared by treating the commercial grade with dry hydrogen chloride at 250 to 300'. A flask containing the material was placed in an oil-bath and kept at that temperature. Hydrogen chloride was passed through for five to six hours. It was then swept clear of any excess by carbon dioxide. This gave the normal salt, whereas the commercial grade is often slightly alkaline, Catalyst.—Hydrogen chloride generated by adding concentrated sulfuric acid to moist sodium chloride was conducted through a sulfuric acid gas-washing bottle into a bottle containing **150** to **200** cc. of the alcohol for which the catalyst was intended. The alcohol used had been purified in the manner described above. After a considerable quantity had bubbled through, it was allowed to come to room temperature. It was then analyzed for chlorine content by the Volhard method. Having determined the concentration of hydrogen chloride in this way, a quantity was diluted up to the proper concentration for the reaction. For convenience, the concentration was so chosen that on adding **1.0** cc. of the catalyst for the reaction mixture, the final concentration was **0.000465** g. of hydrogen chloride per mole of alcohol present. This was the concentration used by Adams. The bottle containing the catalyst thus prepared was protected from the light by covering with glazed paper. It was then inserted into the apparatus as illustrated in Fig. **1.**

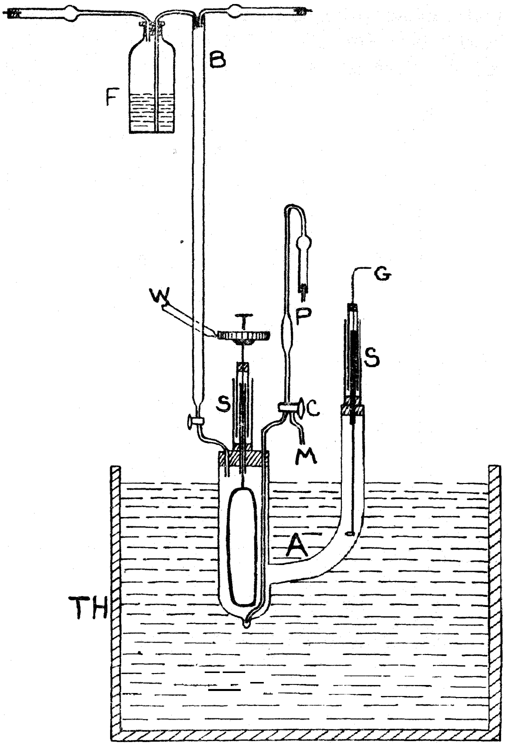


Fig. 1.

It was found that the catalyst diminishes in value as time goes on, if exposed to light, and it seems probable that it does so to a slight extent even when protected. For this reason, the catalyst was always used within a few days after making up. **A** sample unprotected from the light, which contained **0.21107** g. of hydrogen chloride per **10** cc., was found at the end of six weeks of exposure to contain **0.19198** g. per 10 cc. The depreciation, therefore, was about 10% for that period of time. Very probably some of the hydrogen chloride was converted to the alkyl chloride.

The reaction **flask A** in Fig. **1** was kept in the thermostat TH but may be removed independently of the remaining apparatus should accidental breaking of the stirrer T occur or should mercury from either of the seals gain entrance. The stirrer T was propelled by a current of air W working against a fan which **was** attached at the outer end. The **flask A** was washed with three **75cc.** portions of anhydrous alcohol after each experiment. This was introduced through the side arm of A, from which the mercury seal S had been temporarily removed, and was withdrawn through the pipet P into a trap. This procedure was then repeated using 75 cc. portions of anhydrous ether. The pipet P was then connected to a source of air under pressure, the air having been previously passed through a sulfuric acid gas-washing bottle. The air was allowed to pass through at a moderate rate for fifteen to twenty minutes when all of the ether vapors had been removed and the flask was completely dry and filled with an atmosphere of dry air. The aldehyde sample was then put in place in the side arm of A with the finely drawn tip going through the loop of *G*. It was allowed to rest in this position until the alcohol was added. The connection of the mercury seal with the arm was carefully made with collodion. The required quantity of alcohol was forced into the buret B from the flask F by means of an aspirator connected to the drying tube. That part of the buret below its stopcock was filled from the previous experiment. The rubber connections to the drying tubes were shut off by pinchcocks when not in use in order to prevent the action of any vapor from the bottle F upon the calcium chloride in the drying tubes. An identical arrangement for introducing the catalyst was used but is not illustrated by Fig. 1. The alcohol was allowed to flow into the flask. The aldehyde was then released by raising the support G and allowing the tube to fall against the bottom of the arm, thus breaking the capillary tip. The stirrer was working vigorously, meanwhile, so that it was immediately mixed with the alcohol as it flowed into A. In this way the effect of the vapor pressure of the aldehyde on the mercury seals was rapidly diminished. The temperature was allowed to come to 25°. A 5.0cc. sample was then withdrawn into the pipet P through the three-way stopcock C. The sample was allowed to flow into the titration flask F, Fig. 2, through M, Figs 1 and 2.

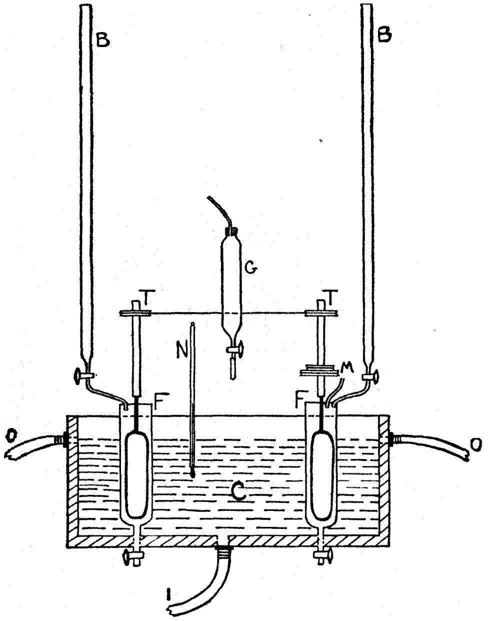


Fig. 2.

The titration flask F, Fig. 2 contained 40 cc. of 10% sodium sulfite maintained at 2 to 3° by a circulating bath C through which ice water was passed in through I and out at O. The aldehyde was determined by titrating the alkalinity developed. This is the Seyewetz-Bardin method described by Child. The amount of alkali formed is equivalent in moles to the available aldehyde and hemiacetal in the sample. The titration flask F on the left was for holding the blank. The stirrers T were operated by a motor at such a speed that good mixing was obtained. The buret G was for measuring out quantities of sodium sulfite from a stock solution immersed in an ice-salt water-bath. The titration must be performed slowly. The acid was allowed to run from the buret B at an average rate of 4 cc. per minute. The volume of liquid in the two flasks was equalized by adding distilled water gradually to the blank so that the temperatures and volumes were identical at the end-point. When the color of the liquid in the two flasks had reached the same degree of intensity when compared by observation against a light background behind the bath C, whose rear and forward faces are of transparent glass, the end-point had been reached and the reading on the buret B on the right was taken.

When the titration for the original concentration had been completed, the catalyst was added through a buret B which was graduated accurately to 0.01 cc. The stirrer T was working vigorously, meanwhile, to insure rapid and thorough mixing. Only 1 cc. of the catalyst was added so that the time consumed never exceeded thirty seconds. The mid-point of this period of time was taken as the initial time in all calculations of the rate. The time was carefully noted by means of a stopwatch with a second hand. Samples were withdrawn at the desired intervals of time and titrated in a manner identical with that described above. The time at which the meniscus of the sample passed a given point on the pipet P, Fig. 1, in discharging, was chosen as the time the sample was taken. Since a titration at the beginning requires ten to fifteen minutes, it was necessary to combine the results of several runs in order to obtain sufficient data for the first hour or so.

The concentrations at the beginning of the reaction were always so regulated that 0.091 mole of aldehyde and 0.000465 g. of hydrogen chloride were present for each mole of alcohol.

It is essential that the reaction mixture be free from mercury. It has been found that mercury diminishes the rate very appreciably.

Summary

The rate of reaction of acetaldehyde with methyl, ethyl, *iso*propyl and *n*-butyl alcohols has been very accurately determined using reagents of very high purity. The curve representing the disappearance of aldehyde is in each case somewhat different for each alcohol so that the quantitative differences between reactivities are somewhat dependent upon the method of comparison. There are, however, no very large differences in the reactivities of the four alcohols for acetal formation.

The values of the reaction velocity constant have been calculated upon the assumption that the reaction under investigation is a bimolecular reversible reaction in which a molecule of hemiacetal reacts with a molecule of alcohol to form a molecule of acetal and of water. The values of k_1 so calculated fall off steadily in the period from 2 to 100 minutes, in some cases to one-tenth of their first value.

The values of the reaction velocity constants have also been calculated upon the assumption that the water formed in the acetal reaction is largely consumed in the hydrolysis of hemiacetal. The constants so obtained are quite consistent after the first few minutes of reaction and a study of them lends confirmation to the assumptions upon which they are based.

The values of the reaction velocity constant for the hydrolytic reaction increase somewhat as the reaction proceeds, but are fairly consistent during the period of 24 to 100 minutes. When the concentration of catalyst used in the hydrolytic reaction is the same as in the synthesis, the reaction rate is very much slower.

The decrease in the velocity constant as the synthesis proceeds, the increase as the hydrolysis proceeds and the lowered rate of hydrolysis as compared with rate of synthesis (in the early stages of each) are all three believed to be due to the poisoning effect of water.

MADISON. WISCONSIN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

OXIDATION IN THE BENZENE SERIES BY GASEOUS OXYGEN III. OXIDATION OF ALPHA PHENYL CARBINOLS

BY H. N. STEPHENS

RECEIVED SEPTEMBER 2, 1927 PUBLISHED JANUARY 6, 1928

In studying the oxidation of alkyl benzenes by gaseous oxygen,[1] the writer has found that methylbenzenes yield as the only identifiable products mono-aldehydes and the corresponding acids, while hydrocarbons containing two or more carbon atoms in the side chain were found to be attacked only at the alpha carbon atom, the products being ketones. In the case of hydrocarbons with secondary alkyl groups, for example, cumene, the reaction involves loss of a methyl group together with the alpha hydrogen. Although a careful search was made in many instances no trace of an alcohol was detected in the oxidation products.

The mere absence of alcohols in the products of oxidation does not, of course, preclude the possibility of their being formed in the reactions, as it might be expected that the oxidation of hydrocarbon to alcohol would require a higher potential than the oxidation of alcohol to aldehyde or ketone. In this event the alcohol would be destroyed as rapidly as it was formed. Preliminary to an attempt to find out whether or not the alcohol stage is an intermediate one in the production of aldehydes and ketones, it was considered desirable to study the oxidation of some α-phenylcarbinols under the same conditions that were employed in the oxidation of hydrocarbons. In this connection an investigation has been made of the oxidation of methyl-, ethyl-, dimethyl-, n-propyl- and isopropylphenylcarbinols.

In examining the products formed from the above alcohols, it was discovered, to our surprise, that no less than three concurrent reactions took place under the conditions employed. Only one of these is a direct oxidation while the other two appear to be thermal dehydrations. These latter will be reported on more fully at a later date, so it will be sufficient for our present purpose merely to mention that one of them involves the elimination of one molecule of water from two molecules of alcohol while the other involves the loss of a molecule of water from each molecule of alcohol. The structural nature of the products of the first type of dehydration is not yet fully established but in the second type unsaturated hydrocarbons are produced.

Oxidation Products

All the secondary alcohols employed, with the exception of isopropylphenylcarbinol, underwent direct oxidation to a very limited extent, yielding small amounts of the corresponding ketones. Ethylphenyl- and

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[1] Stephens, THIS JOURNAL, 48, 1824, 2920 (1926).

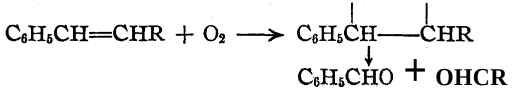
n-propylphenylcarbinols were found to be the most readily oxidized, methylphenylcarbinol was attacked very much less and, strange to say, isopropylphenylcarbinol was unaffected at the temperature used.

Although in the oxidation of the secondary alcohols a simple oxidation of the —CHOH— group to —CO— may take place, when tertiary alcohols are concerned (for example, dimethylphenylcarbinol) an alkyl group must be destroyed before a ketone can be formed. As acetophenone is a product in the oxidation of dimethylphenylcarbinol, this is probably what takes place, the oxidation being analogous to that of cumene,[1] the corresponding hydrocarbon, which also yields acetophenone. However, on account of there being another way (see below) in which acetophenone may be formed from dimethylphenylcarbinol, it is impossible to determine to what extent direct oxidation takes place or, indeed, whether it **takes** place at all.

Secondary Oxidations

It has been mentioned that unsaturated hydrocarbons were produced by dehydration of the carbinols under the conditions employed. With the exception of one instance, that of the production of *iso*propenylbenzene from dimethylphenylcarbinol, no hydrocarbons were detected in the final products as they were destroyed by oxidation as rapidly as they were formed. The fact that they are actually formed from the secondary alcohols, as well as from dimethylphenylcarbinol, was demonstrated by heating a sample of ethylphenylcarbinol in an atmosphere of carbon dioxide at 102–104° for ten days, at the end of which time quite an appreciable amount of unsaturated hydrocarbon was detected. In the case of dimethylphenylcarbinol, the speed of dehydration was evidently much greater than the speed of oxidation of the product; consequently a considerable amount of hydrocarbon survived.

It is well known that in some cases auto-oxidation of substances containing the ethylenic linkage involves scission of the molecule at the double bond and by assuming this type of reaction to take place, **all** oxidation products isolated in the oxidation of carbinols can be satisfactorily accounted for. Considering the hydrocarbons that would result from the dehydration of the secondary carbinols, the following general equations would represent the oxidations that could take place



$$C_6H_5CH{=}CHR + O_2 \longrightarrow \overset{\qquad\quad O\text{———}O}{C_6H_5CH\text{———}CHR}$$
$$\downarrow$$
$$C_6H_5CHO + OHCR$$

and

$$2C_6H_5CHO + O_2 \longrightarrow 2C_6H_5COOH$$

Benzaldehyde was actually isolated in only one oxidation, that of ethylphenylcarbinol, but its oxidation product, benzoic acid, was isolated in the oxidation of ethylphenyl-, n-propylphenyl- and *iso*propylphenylcarbinols. A small amount of solid acid was also obtained from methylphenylcarbinol but this was insufficient for purification. The second aldehyde which would be expected from scission of the peroxide was never isolated, as it was probably lost by volatilization or, in the case of formaldehyde, by oxidation,[2] under the conditions of the experiments.

On the above basis isopropenylbenzene (from dimethylphenylcarbinol) would be expected to yield, as oxidation products, acetophenone and formaldehyde. On oxidation of the hydrocarbon alone at 102–104°, acetophenone was formed, while the formaldehyde was lost by volatilization. On account of the fact that acetophenone is formed from the dehydration product of dimethylphenylcarbinol and is also probably a product of the direct oxidation of the alcohol, it is impossible to determine the extent of direct oxidation, if it takes place at all.

The Inhibitory Action of Water

In the presence of excess water all three reactions mentioned above are completely inhibited. In view of the fact that each reaction involves the elimination of water, the most obvious explanation of this surprising inhibitory effect might lie in the assumption that all are reversible. In the two dehydrations which take place, it is not difficult to understand how the elimination of water might be a strictly reversible reaction, but in the case of direct oxidation of the alcohol, the way is not so clear. In the earlier papers on the oxidation of hydrocarbons to aldehydes or ketones, it has been assumed that oxidation consists of more than one stage, one of these being a reversible reaction involving the elimination of the elements of water. In the oxidation of carbinols it seems necessary to make a similar assumption.

Further work on the mechanism of these reactions is in progress and an investigation of the reversibility of the two dehydrations of carbinols is also planned.

Experimental Part

Materials.—The carbinols employed in the research were all synthesized by means of the Grignard reaction. The secondary carbinols were prepared from benzaldehyde with methylmagnesium iodide, ethylmagnesium bromide and n-propyl- and isopropylmagnesium chlorides. Dimethylphenylcarbinol was prepared from phenylmagnesium bromide and acetone.

In purifying the secondary carbinols the unchanged benzaldehyde was first carefully removed by allowing the product to stand over saturated bisulfite solution. This was repeated with fresh portions of bisulfite until no precipitate formed on standing for twenty-four hours. After washing the residual liquid with several small portions of the solution and finally

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[2] Ref. 1, p. 2921.

with potassium carbonate solution, it was dried over anhydrous potassium carbonate and fractionated under reduced pressure. Distillations were repeated until a product was obtained which boiled within 1°. The first two or three drops of each final distillate gave no test for carbonyl compounds with semicarbazide hydrochloride and potassium acetate in aqueous alcohol solution.

Procedure.—The crude product of oxidation was in each case examined for benzaldehyde, benzoic acid and a ketone. The benzaldehyde was removed by allowing the liquid to stand for at least forty-eight hours over a small portion of saturated sodium bisulfite solution. Only in the case of ethylphenylcarbinol was a precipitate of addition compound obtained and this was decomposed with sodium carbonate and the aldehyde characterized as the semicarbazone. When no precipitate was obtained the bisulfite was neutralized with sodium carbonate, partially distilled and the distillate treated with semicarbazide hydrochloride and potassium acetate, but no semicarbazone was detected in any of these instances.

Benzoic acid was removed by treating the residue from the bisulfite treatment with sodium bicarbonate solution and later acidifying with dilute hydrochloric acid. Finally, the liquid was dried over anhydrous potassium carbonate and submitted to fractional distillation under reduced pressure. As ketones always boil at a lower temperature than the corresponding alcohols, the lower fractions were collected and these treated with semicarbazide hydrochloride and potassium acetate in aqueous alcohol solution.

Methylphenylcarbinol

I. Twenty-five g. of methylcarbinol, b. p. 85–86' (7 mm.), treated with dry oxygen for ten days at 102–104° yielded 2.1 g. of a liquid, b. p. 132–136' (7 mm.), and a very small amount of acetophenone, isolated as the semicarbazone (m. p. 201°[3]), m. p. 201°.

II. Twenty-five g. of methylphenylcarbinol, oxidized for eleven days at 122–124°, yielded about 8 g. of liquid, b. p. 132–136° (7 mm.), 0.85 g. of acetophenone and a trace of a solid acid, presumably benzoic.

Action of Water.—Twenty-five g. of methylphenylcarbinol and 25 g. of water, treated at the boiling point with oxygen for twelve days, yielded no reaction product.

Ethylphenylcarbinol

Twenty-five g. of ethylphenylcarbinol, b. p. 105–106° (17 mm.) oxidized for ten days at 102–104°, yielded 10 g. of a liquid, b. p. 158–160° (12 mm.), 0.21 g. of benzoic acid, m. p. 121°, 0.34 g. of ethylphenyl ketone, isolated as semicarbazone,' and a very small amount of benzaldehyde, identified as its semicarbazone by the mixed melting point method.

Action of Heat in an Inert Atmosphere.—Twenty-five g. of ethylphenylcarbinol heated to 102–104° in an atmosphere of carbon dixoide, yielded a considerable amount of

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[3] Klages, Ber., 37, 2306 (1904).

[4] The melting points given in the literature for the semicarbazone of ethylphenyl ketone vary from 173–175° to 182°. The writer has found that rate of heating influences the melting point considerably. The highest melting point obtained was 179°.

unsaturated hydrocarbon and 9.5 g. of an oil, b. p. 158–160° (12 mm.). Assuming the hydrocarbon to be propenylbenzene, the absorption of bromine in carbon tetrachloride solution would indicate its presence to the extent of approximately 0.25 g.

Action of Water.—Forty g. of ethylphenylcarbinol plus 40 g. of water yielded no reaction product in detectable quantity.

Dimethylphenylcarbinol

Forty g. of dimethylphenylcarbinol, b. p. 79–80° (7 mm.), oxidized for ten days at 102–104" yielded 3.2 g. of an unsaturated hydrocarbon, b. p. 159–161°, 12 g. of a high-boiling liquid, b. p. 158–162° (8 mm.), and a very small amount of acetophenone, identified as semicarbazone, m. p. 201'. The unsaturated hydrocarbon, oxidized alone at 102–104°, yielded acetophenone as a product. It is, therefore, *iso*propenylbenzene, b. p. 161–162°.[5] The other product, formaldehyde, which would be expected from the oxidation of this hydrocarbon, could not be detected, as it would be volatilized under the conditions employed.

Action of Water.—Twenty-two g. of dimethylphenylcarbinol plus 22 g. of water, treated with oxygen for twelve days at the boiling point, yielded no reaction product.

n-Propylphenylcarbinol

Twenty-five g. of n-propylphenylcarbinol, b. p. 107–108° (8.5 mm.), oxidized for ten days at 102–104° yielded 10.5 g. of a liquid b. p. 173–175° (12 mm.), a small amount of benzoic acid, m. p. 120–120.5°, and 0.76 g. of n-propylphenyl ketone, isolated as semicarbazone (m. p. 188.5°[6]), m. p. 188".

Action of Water.—Fifteen g. of n-propylphenylcarbinol plus 15 g. of water, treated with oxygen for ten days at the boiling point, yielded no product.

*iso*Propylphenylcarbinol

Twenty-five g. of isopropylphenylcarbinol, b. p. 97.5–98.5° (9 mm.), oxidized for ten days at 102–104° yielded 9 g. of a liquid, b. p. 163–164" (12 mm.), and a very small amount of benzoic acid, m. p. 119–120° (recrystallized once), but no ketone.

Summary

The oxidation by gaseous oxygen of several a-phenylcarbinols has been studied and it has been found that only a very small proportion of the substances undergo direct oxidation to ketones.

Two other reactions take place under the conditions employed, both of which appear to be thermal dehydrations. One of these results in the formation of high-boiling liquids, which correspond to two molecules of carbinol minus one molecule of water. This latter is the main type of reaction that takes place. The other dehydration yields unsaturated hydrocarbons.

All three types of reactions are completely inhibited in the presence of excess water.

Work on the mechanism of these reactions is being continued in this Laboratory.

MINNEAPOLIS MINNESOTA

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[5] Tiffeneau, Ann. *chim.*, [8] 10, 157 (1907).

[6] Sorge, Ber., 35, 1074 (1902).

[CONTRIBUTION FROM RESEARCH LABORATORIES, E. R. SQUIBB & SONS]

STUDIES ON THE ANALYSIS AND CHEMISTRY OF NEOARSPHENAMINE[1]

BY ALFRED E. JURIST AND WALTER G. CHRISTIANSEN

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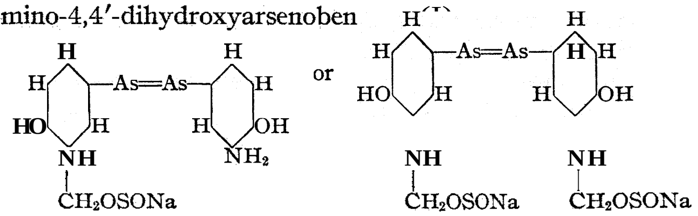
Weoarsphenamine is officially described as a condensation product of 3,3'-diamino-4,4'-dihydroxyarsenoben



I

and sodium formaldehyde sulfoxylate. Since it is not a pure crystalline substance but a complex mixture of varying composition, an accurate method of analysis is important in making a synthetic study. Investigation of the available methods showed that of Elvove[1a] most satisfactory. However, it was found necessary to make two modifications, and as a result of these two modifications of Elvove's method it is possible to gain a clearer insight into the composition and chemistry of neoarsphenamine than has been possible hitherto.

The Elvove method of analysis is based on a differential sulfur determination, chiefly on the assumption that the combined and free sodium formaldehyde sulfoxylate differ in their reaction to iodine in neutral[2] solution in that the free sulfoxylate only reduces iodine in neutral solution whereas both the free and combined sulfoxylate reduce iodine in alkaline solution. Freedman[3] calls attention to the fact that this is not correct and we have found that the combined sulfoxylate as well as the free sulfoxylate reduces iodine in neutral solution. This can be demonstrated by oxidizing neoarsphenamine with an excess of iodine, reducing the excess iodine with sodium arsenite, acidifying the solution and then precipitating the sulfur as barium sulfate instead of titrating the excess iodine with sodium thiosulfate as in the Elvove method. The sulfur thus determined directly as barium sulfate is usually greater than that calculated by the Elvove method.

Free sodium formaldehyde sulfoxylate reduces 4 atoms of iodine, whereas combined sodium formaldehyde sulfoxylate reduces only 2 atoms of iodine.

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[1] This paper was presented before the American Chemical Society, Section on Chemistry of Mechanical Products, at Detroit, in September, 1927.

[1a] Elvove, *U. S. Pub. Health S. Repts.*, *40*, 1235 (1925).

[2] The P_H of neoarsphenamine solutions varies from 5.8 to 9.0.

[3] Freedman, *J. Lab. Clin. Med.*, *11*, 6 (1926).

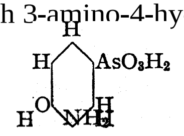
By applying these facts and the results obtained by the method just described, which we shall call the arsenite method to distinguish it from the Elvove direct titration, along with the Mvove titration two simultaneous equations may be set up, as follows

$$x + y = A; \frac{x}{0.8} + \frac{y}{1.6} = B$$

where x is the free sulfoxylate sulfur, y the combined sulfoxylate sulfur, A the sulfur found by the arsenite method less the free sulfate sulfur and B the iodine titration in neutral solution corrected for the arseno group iodine equivalent. These equations give directly both the free and combined sulfoxylate sulfur.

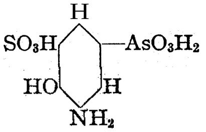
In addition to the free and combined sulfoxylate sulfur determinations, Elvove uses a free sulfate sulfur determination and a total sulfur determination. The difference between the total sulfur and the sulfur oxidizable by iodine in alkaline solution, the total sulfoxylate sulfur, is then considered to be sulfur present as sulfarsphenamine. It has been found that this sulfur difference represents not sulfarsphenamine but nuclear sulfur introduced in the preparation of the arsphenamine base from which the neoarsphenamine was prepared.

In order to demonstrate this, two preparations of arsphenamine base were made in which great care was taken to avoid the introduction of nuclear sulfur by starting with 3-amino-4-hydroxyphenylarsonic acid (II),



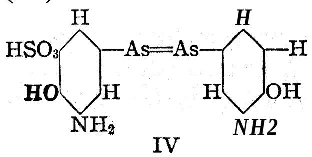
II

which has been shown by Christiansen[4] to yield a base low in nuclear sulfur, but in one of these preparations 10% of 3-amino-4-hydroxy-5-sulfophenylarsonic acid (III)



III

was substituted for the "amino" acid, yielding a base containing 10% of the sulfonic acid derivative (IV)



IV

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[4] (a) Christiansen, This journal, 43, 2202 (1921); 44, 2334 (1922).

The two bases so obtained were analyzed for sulfur and arsenic and then converted into neoarsphenamines, using formaldehyde sulfoxylate which was known to be free from formaldehyde bisulfite. The neoarsphenamines were than also analyzed for total sulfur and sulfur oxidizable by iodine in alkaline solution. The results of the sulfur analyses of the neoarsphenamines and the bases from which they were made are as follows:

Sulfur content of base made free from sulfonic acid . . .	1.51%
Sulfur content of base with 10% of sulfonic acid	2.31%
Calculated sulfur due to sulfonic acid.	0.77%
Sulfonic acid sulfur found.	.80%
Nuclear sulfur content of neoarsphenamine made from base free from sulfonic acid.	.06%
Calculated sulfur content of neoarsphenamine made from base with 10% sulfonic acid.	.53%
Found sulfur content of neoarsphenamine made from base with 10% sulfonic acid.	.57%

These results serve to demonstrate conclusively the fact that the "sulfarsphenamine sulfur" of Elvove is actually nuclear sulfur.

A further addition to the methods given here permits the determination of the percentage composition of neoarsphenamine by utilizing the results of the differential sulfur determinations, the arsenic content and several factors as follows:

The per cent. of sulfoxylate sulfur × 3.69 = % of free sulfoxylate
The per cent. of combined sulfoxylate sulfur as mono-substituted arsenical ÷ 6.87 = % of mono-substituted arsenical
The per cent. of combined sulfoxylatesulfur as di-substituted arsenical ÷ 11.31 = % of di-substituted arsenical
(The per cent. of arsenic—the per cent. of arsenic as substituted arsenical) × 2.44 = % of free base
The per cent. of free sulfate sulfur × 4.44 = % of sodium sulfate

A large number of neoarsphenamines have been analyzed by the foregoing methods and the results so obtained are given in the following table, showing examples of some of the different types observed.

The results given here show a great difference between the results given by the Elvove method and by the arsenite method for determining free and combined sulfoxylate sulfur. In types A and B, the free sulfoxylate sulfur is always less by the arsenite method than by the Elvove method and the combined sulfoxylate sulfur always greater. In certain cases, namely, type C, the amount of combined sulfoxylate sulfur is small by the Elvove method, but still less by the arsenite method, there being none in two instances. This latter result is not a fault, however, in the method but rather an indication of the existence of a type of combination between arsphenamine base and sulfoxylate differing from that usually described, a probability which must be assumed since the Elvove and arsenite methods both

TABLE I

RESULTS OF ANALYSES

Number[a]	% Arsenic	% Total sulfur	% Sulfur oxidizable by iodine in alkaline solution (Elvove)	% Nuclear sulfur	% Free sulfate sulfur	% Free sulfoxylate sulfur (Elvove)	% Free suifoxylate sulfur (arsenite)	% Combined sulfoxylate sulfur (Elvove)	% Combined sulfoxylate sulfur (arsenite)	% Non-sulfoxylate sulfur [3 − (7 + 9)]	% Sulfur required for mono-substitution calcd. on % of arsenic	% Free sulfoxylate	% Mono-substituted arsenical	% Di-substituted arsenical	% Free arsphenamine base	% Sodium sulfate	% Inert matter
Column no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
A-1-P	21.53	6.14	6.00	0.	.48	3.42	149	2.13	3.87	0.19	4.59	5.37	56.32	0.00	8.26	2.13	27.92
A-2-P	20.84	6.80	5.81	.99	.64	3.73	196	1.44	3.54	.31	4.45	7.23	51.52	.00	10.37	2.84	28.04
A-3-P	22.06	6.76	6.50		.77	3.54	157	2.	3.93	.23	4.71	5.79	57.20	.00	8.88	3.42	24.71
A-4-P	19.53	6.88	6.61	.27	1.14	4.20	336	1.27	1.68	.43	4.17	12.40	24.45	.00	28.46	5.06	29.63
B-1-E	24.39	9.13	9.08		.66	4.18	.46	4.	7.43	.53	5.20	1.70	43.23	39.46	0.00	2.93	12.68
B-2-E	27.82	8.64	7.83		.38	3.90	.34	3.	7.11	.00	5.93	1.25	69.13	20.88	.00	1.69	7.05
B-3-P	19.53	8.88	8.57		1.22	2.92	.00	4.43	6.43	.92	17	.00	27.80	39.99	.00	5.42	26.79
B-4-E	27.25	8.92	8.08		1.19	2.98	.05	3.92	5.85	1.00	5.81	.19	83.97	0.70	.00	5.28	19.86
C-1-P	19.35	7.66	7.37		.87	5.77	5.41	0.73	0.72	0.37	4.13	19.96	10.48	.00	38.78	3.86	26.92
C-2-P	20.24	8.07	7.92		1.06	5.38	5.18	1.48	.41	1.27	4.22	19.12	5.97	.00	44.71	4.71	25.49
C-3-P	19.70	9.30	8.25	1	1.10	6.62	6.62	0.53	.00	0.53	4.20	24.43	0.00	.00	48.08	4.88	22.61
C-4-P	19.49	8.42	8.61	.00	0.78	7.05	6.79	.78	.00	1.04	4.16	25.06	.00	.00	47.56	3.46	23.92

[a] P = commercial product, = experimental product.

sometimes give results for the combined sulfoxylate which are almost impossibly low.

The directly detectable difference between the two types of combined sulfoxylate sulfur is their reaction to iodine in neutral solution in which the usual or N-methylene type of combined sulfoxylate reduces but two atoms of iodine whereas the second type of combined sulfoxylate reacts in the same manner as free sulfoxylate and reduces four atoms of iodine. This latter type of combined sulfoxylate can be explained on the basis of a double salt of arsphenamine base and sulfoxylate similar to the metallic compounds of arsphenamine, such as the silver compound, due, perhaps, to reactions of secondary valences of the arseno linkage or the amino group. While this possibility has previously been expressed verbally to one of us, this is the first evidence presented to support this view and the results also show the possibility of the existence of both types of combined sulfoxylate in one product.

In addition to the differences between the amounts of free and combined sulfoxylate sulfur given by the Elvove method and the arsenite method, the latter shows the presence in neoarsphenamine of a type of sulfur hitherto unrecorded. This is here called the non-sulfoxylate sulfur and varies in these analyses from 0.19 to 1.27%. No information is available as to the nature of this sulfur but it probably has its origin in decomposition or reaction with the benzene ring of the sulfoxylate used in the preparation of neoarsphenamine. However, several preparations which were exposed to air contained large amounts of non-sulfoxylate sulfur, indicating that it may be an oxidation product. While the nature of this sulfur is not clearly indicated, it can be oxidized to sulfate by iodine in alkaline solution but not in neutral solution so that the amount can be determined by subtracting the total arsenite sulfur from the sulfur oxidized to sulfate in alkaline iodine solution.

In the foregoing data it will be noted that there is a wide range of variation in the nuclear sulfur from zero to 1.05%. This indicates clearly to what extent the variation in nuclear sulfur can occur with slight variations in the base, but in only four instances is this nuclear sulfur present in amounts greater than 0.31%.

The data showing the compositions of the neoarsphenamines illustrated disclose a wide range of variation in composition from products which have no sulfoxylate directly condensed on the amino group to products which contain more di-substituted arsenical than mono-substituted arsenical. The free sulfoxylate varies from zero to 25.00% and many of the products examined contain at least small amounts of arsphenamine base. All neoarsphenamines examined contain a small amount of sodium sulfate introduced as an impurity in the sulfoxylate used in their preparation.

Summary

The method of analysis given here leads to a fairly complete knowledge of the composition of neoarsphenamine and it has been found:

1. That the arsenite method of analysis gives a more accurate distribution of the sulfur in neoarsphenamine than has been previously possible.
2. That the so-called "sulfarsphenamine sulfur" is, in fact, nuclear sulfur.
3. That there are probably two types of combination between arsphenamine base and sodium formaldehyde sulfoxylate, one being of the N-methylene type, and the other resembling a double salt formation.
4. That there is a type of sulfur present in neoarsphenamine which owes its origin to some reaction or decomposition of sodium formaldehyde sulfoxylate but it is no longer present as sulfoxylate.

BROOKLYN, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

THE DIBROMIDES OF METHYLCOUMARIC AND METHYLCOUMARINIC ACIDS

BY MARIE REIMER AND MARION HOWARD

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In connection with a study of o-methoxybenzalpyruvic acid it became necessary, for purposes of identification, to prepare α-bromo-*o*-methoxycinnamic acid (169–171°). As reactions for the preparation of this substance by the action of a 50% aqueous solution of potassium hydroxide on methylcoumaric acid dibromide, according to the directions of Perkin,[1] failed to give the substance he described, we have made a study of the action of bromine on methylcoumaric and methylcoumarinic acids and of the elimination of hydrogen bromide from the resulting compounds. Perkin[1] described two isomeric dibromo addition products, neither of which, however, he prepared in the pure condition. Fittig and Ebert[2] questioned Perkin's results, as they were able to obtain but one dibromo compound. Later investigators[3,4,5] were also unable to identify two products of the reaction, although Stoermer mentions an "impure methylcourmarinic dibromide" left in the filtrates. We find that the product of addition of bromine to methylcoumaric and methylcoumarinic acids is in each case a mixture of isomers which we have succeeded in separating and purifying; a dibromo acid melting, with vigorous decomposition, at 177° and, in smaller quantity, an isomeric acid melting, with very slight de-

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[1] Perkin, *J. Chem. Soc.*, 39, 418 (1881).

[2] Fittig and Ebert, Ann., 216, 146 (1883).

[3] Werner, *Ber.*, 39, 27 (1906).

[4] Stoermer and Friemel, *Ber.*, 44, 1838 (1911).

[5] Biilmann and Lund, *Ann. chim.*, [9] 18, 263 (1922).

composition, at 134° and changing above this temperature to the higher-melting isomer.

The isomeric dibromo acids differ markedly in solubility and in their behavior toward alkaline reagents. The higher-melting acid reacts rapidly with 50% aqueous potassium hydroxide, the chief product of the reaction being an oil which was proved to be a-bromo-o-methoxystyrene. This was accompanied by a very small amount of the potassium salt of an acid melting when pure at 136°, instead of a large percentage of acid melting at 169–171° as was expected from Perkin's description of this experiment. This low-melting acid was the chief product of the reaction when alcoholic instead of aqueous potassium hydroxide solution was used with the dibromo acid (177°). The dibromo acid (134°), treated with 50% aqueous potassium hydroxide, reacted slowly in the cold to give an almost quantitative yield of an acid melting at 171°, the same α-bromo-*o*-methoxycinnamic acid as described by Perkin (169–171°). That this acid is the geometrical isomer of that melting at 136° is proved by the ready conversion of the latter into the acid (171°) by exposure of its aqueous solution to the sunlight.

Since it was found possible to prepare the two dibromo acids in pure condition and since they differ so markedly toward alkaline reagents, it seemed of interest to carry out with both acids certain of the reactions previously studied by other investigators with the higher melting of the two. The products of the reactions of the two dibromo acids with water and with an aqueous solution of bromine were the same. With methyl alcohol isomeric compounds have been obtained.

Experimental Part

Preparation of Methylcoumaric and Methylcoumarinic Acids

Since coumarin is the least expensive of the substances from which these compounds can be prepared and dimethyl sulfate, for the same reason, is to be preferred to methyl iodide, a modification of the method of Stoermer and Friemel was used instead of that of Reychler[6] which gives better yields.

Fifty grams of coumarin was dissolved by warming with a solution of 30 g. of sodium hydroxide in 150 cc. of water. To the cooled solution 100 g. of dimethyl sulfate was added, the mixture shaken repeatedly and allowed to stand at room temperature for about three days. At the end of this time an oil, the methyl ester of methylcoumarinic acid, had separated. Water was added until the ester formed the lower layer; it was drawn off, the ethereal extract of the aqueous residue added to it, the ethereal solution washed repeatedly, dried over calcium chloride, and the ether distilled off. The clear oil remaining was hydrolyzed by boiling with 30% potassium hydroxide solution if methylcoumarinic acid was to be prepared or distilled

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[6] Reychler, *Bull. soc. chim.*, [4] 3, 551 (1908).

and then hydrolyzed to obtain methylcoumaric acid. The change of the methyl ester of methylcoumarinic acid to that of methylcoumaric acid on distillation was not complete but a fair yield of the latter could be obtained by rapid and repeated distillation. Although a boiling point of 275" is given as that of the methyl ester of methylcoumarinic acid, hydrolysis of the fraction distilled carefully at this temperature gives a mixture of the two acids. This agrees with the results of Biilmann. By rapid distillation the boiling point rises to 293°, that of methylcoumaric acid methyl ester. The yield of methylcoumarinic acid (m. p. 92–93") obtained by hydrolysis of the undistilled ester was 78% calculated from the coumarin used; that of methylcoumaric acid (m. p. 182") obtained from the ester two or three times distilled was 40 to 50%.

Action of Bromine on Methylcoumarinic and on Methylcoumaric Acids

Methylcoumarinic acid was dissolved in carbon disulfide, the calculated amount of bromine added slowly to the cooled solution and the solvent evaporated completely in a current of air. The pure white dibromo addition product, formed in quantitative yield, softened slightly at 120 to 130° and melted with decomposition at about 165". Twenty-two grams of this product was treated with 25 cc. of toluene and the mixture thoroughly heated with stirring in boiling water. The liquid was drawn off, the undissolved residue extracted again at 100° with 25 cc. of toluene and a third time with 20 cc. The undissolved portion melted at 174–175°; on crystallization from boiling toluene it separated in compact clumps, melting with vigorous decomposition at 177°. The crystals that separated from the three toluene extracts were those of the impure, low-melting dibromide. They were purified by treatment at 100° with a quantity of toluene insufficient for complete solution; the portion undissolved was impure, high-melting dibromide. The crystals separating from the solution were again treated in the same way until after four or five recrystallizations the substance had a constant behavior on melting. The pure, low-melting dibromide melts to a clear liquid at 134" and immediately resolidifies; this solid begins to give off a gas at 169° and clears and decomposes vigorously at 170°. The melting at 134° is accompanied by slight decomposition, so that the final melting point is never as high as that of the pure high-melting isomer. That this behavior in the melting point tube is due to a transformation to the high-melting isomer was proved by heating a considerable quantity of the low-melting acid for about ten minutes to 136°. The cooled product, slightly brown, after washing with warm toluene melted at 177° and at the same temperature when mixed with the pure, high-melting dibromo acid.

Anal. (Subs. 134°.) Subs., 0.1794, 0.1446: CO_2, 0.2326, 0.1888; H_2O, 0.0523, 0.0396. Calcd. for $C_{10}H_{10}O_3Br_2$: C, 35.52; H, 2.96. Found: C, 35.36, 35.59; H, 3.23, 3.03. Subs. 7.628 mg.: AgBr, 8.588 mg. Calcd.: Br, 47.33. Found: 47.84 (micro-Carius). Subs. 8.434 mg.: AgI, 5.820 mg. Calcd.: OCH_3, 9.17. Found. 9.22 (micro-Zeisel).

The quantity of pure acid (134') isolated from the reaction of bromine on methylcoumarinic acid was 18 to 20% of the crude product; by the action of bromine on methylcoumaric acid no more than 9 to 10% was obtained. The substance crystallizes from toluene in clumps of branching needles which separate on the surface of the solution and "creep" up the sides of the beaker, a behavior characteristic of this isomer as distinguished from that of the other. In fact it is possible to make a rough separation of the isomers by allowing a toluene solution of the mixture to stand until the solvent has completely evaporated. The crystals on the sides and over the top of the beaker are slightly impure, low-melting acid; the compact crystals on the bottom, the high-melting form. The low-melting acid is not as stable as its isomer but takes on a brown coloration on exposure to light and air.

The solubilities of the two dibromo acids in the solvents which have been used by other investigators of this bromination reaction are given in the following table.

Table I

Solubilities

Substance	G. of subs. in 100 g. solvent			
	CS_2 (20°)	$CHCl_3$ (20°)	Toluene (209	Toluene (100°)
177°	0.33	3.73	2.08	**6.91**
134°	1.54	14.50	4.88	**45.91**

It is evident that for the separation of these isomers toluene at 100° is the best solvent. The compound (134°) can be heated in toluene at **100°** for many hours without isomerization. In boiling toluene, however, it gradually changes to the high-melting form. This fact, together with the decidedly greater solubility of the 134" acid, evidently accounts for the failure of other investigators to isolate the compound.

Reaction of Alkalies on the Dibromo Acids

a-Bromo-o-methoxycinnamic Acid, 2-$CH_3OC_6H_4CH{=}CBrCOOH$ (171°).—When finely ground crystals of the acid (134") were stirred in an excess of a 50% aqueous solution of potassium hydroxide, the crystals became opaque and slowly went into solution; after standing for twenty-four hours an almost solid mass of a colorless potassium salt had separated. This was filtered out and dissolved in water. **A** faint cloudiness due to the oil, α-bromo-*o*-methoxystyrene, was removed by filtration. Addition of hydrochloric acid precipitated a colorless acid which separated from boiling water in long, fine needles melting at 171°. The acid is in all respects like that described by Perkin as melting at 169–171°. From the solution left after filtration of the potassium salt, more of the same acid was precipitated. The yield was practically quantitative. By boiling the acid with 10% aqueous potassium hydroxide solution, a second molecule of hydrogen bromide was eliminated readily and *o*-methoxyphenylpropiolic acid (124–125°) formed, as described by Perkin.

α-Bromo-*o*-methoxycinnamic Acid (136°).—The dibromo acid melting at 177° was subjected to the same treatment as that described above. After twenty-four hours, the solution was clear except for a few crystals of a potassium salt. These, on solution and acidification, gave a trace of an acid melting at about 130°. On acidification of the potassium hydroxide solution, an oil separated. It was taken up with ether, the ethereal solution washed with sodium carbonate, dried, the ether distilled off and the residue, a pale yellow, fragrant oil, analyzed.

Anal. Subs. 0.1112; CO_2, 0.2069; H_2O, 0.0405. Calcd. for C_9H_9OBr: C, 50.70; H, 4.22. Found: C, 50.74; H, 4.04.

The substance on oxidation with potassium permanganate in the cold yields o-methoxybenzoic acid. It is, therefore, a-bromo-o-methoxystyrene, 2-$CH_3OC_6H_4CH{=}CHBr$.

In the hope of getting a larger quantity of the low-melting acid, the dibromo acid (177°) was treated with potassium hydroxide in alcoholic solution; **3** g. of the finely powdered acid was covered with a saturated solution of potassium hydroxide in methyl alcohol and the mixture stirred vigorously. Soft, white crystals began to separate immediately and after three minutes there was a nearly solid mass of this substance. The solid, a potassium salt, was at once filtered and dissolved in water, a trace of bromostyrene filtered out and the cooled solution acidified. The mixture, at first cloudy, rapidly deposited pale yellow needles of an acid which was purified by crystallization from hot benzene It separates in stiff, pale yellow needles melting at 136'; from hot water it separates in a pasty condition and slowly solidifies.

Anal. Subs. 0.1577, 0.1690; CO_2, 0.2692, 0.2897; H_2O, 0.0531, 0.0553. Calcd. for $C_{10}H_9O_3Br$: C, 46.68, H, 3.50. Found: C, 46.49, 46.66; H, 3.75, 3.63.

The yield of this acid was 80–90% of that calculated. From the aqueous filtrates a small amount of a higher-melting, colorless acid separated slowly. This was formed by the action of light on the solution of the yellow acid (136°) as was proved by subjecting a saturated aqueous solution of the latter in a quartz test-tube to bright sunlight. After two hours the liquid was filled with a mass of fine, white needles. This substance crystallized from hot water in long, stiff needles melting at 171°. A mixed melting point determination proved it to be identical with the a-bromo-o-methoxycinnamlc acid (171°) previously described. This transformation shows that the new, more soluble yellow acid (136°) is the geometrical isomer of the slightly soluble, colorless acid (171°). The same transformation can be brought about in benzene solution.

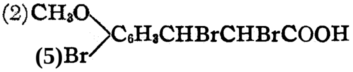
The methyl ester of the acid (136°) could not be prepared by allowing the acid to stand in contact with methyl alcohol saturated with hydrogen chloride; almost the whole amount of the acid was recovered unchanged after many hours. The pure ester, a lemon-yellow, mobile oil, was prepared in quantitative yield by the action of diazomethane on the purified acid.

Anal. Subs. 0.1311; CO_2, 0.2342; H_2O, 0.0499. Calcd. for $C_{11}H_{11}O_3Br$: C, 48.70; H, 4.05. Found: C, 48.64; H, 4.23.

Elimination of hydrogen bromide from the acid (136°) was much more difficult than from the isomeric acid. After boiling a solution of the acid in 10% potassium hydroxide solution for thirty minutes, practically the entire amount was recovered unchanged. After boiling the solution for two hours, the acetylenic acid was precipitated from the acidified solution together with a considerable quantity of methoxybromostyrene.

The differences in properties of the two isomeric acids might indicate that the acid (136°) is the cis, the acid (171") the trans isomer but no conclusion can be.drawn without direct experimental evidence.

Reaction of Aqueous Bromine Solution on the Two Dibromo Acids

5-Bromo-2-methoxycinnamic Acid Dibromide, 

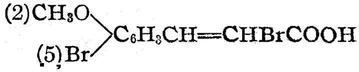
$$\left.\begin{matrix}(2)CH_3O\\(5)Br\end{matrix}\right\rangle C_6H_3CHBrCHBrCOOH$$

(201").—The dibromo acid (177") on treatment with an aqueous solution of bromine, according to the directions of Biilmann,[5] gave a practically quantitative yield of a product with a bromine atom in the ring. After crystallization from benzene it melted at 201". (M. p. given by Biilmann, 198°; Perkin, 188°.)

The dibromo acid (134°), subjected to the same treatment, became pasty and even on vigorous shaking could not be made to react completely with the bromine solution. The only product isolated melted at about 184" and was shown by analysis to be a mixture of a tribromo and a dibromo compound. By repeated recrystallization of this mixture a small amount of the tribromo acid (201°) was obtained in pure condition.

By the action of hot aqueous potassium hydroxide solution on this tribromo acid, Perkin obtained 5-bromo-2-methoxyphenylpropiolic acid. By a less strenuous method we have prepared two isomeric ethylenic acids.

α-Bromo-5-bromo-2-methoxycinnamic Acid,



$$\left.\begin{matrix}(2)\mathrm{CH_3O}\\(5)\mathrm{Br}\end{matrix}\right>\mathrm{C_6H_3CH{=}CHBrCOOH}$$

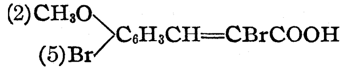
(163–164°).—Two grams of the tribromo acid was covered with a saturated solution of potassium hydroxide in methyl alcohol and the mixture stirred. The tribromo acid dissolved at once and a very few crystals of a potassium salt separated. After five minutes, addition of water produced no cloudiness, indicating that there had been no formation of a styrene derivative as was the case with the acids in which there was no bromine in the ring. Acidification of the solution gave a pasty precipitate which slowly solidified after cooling and vigorous stirring. The substance, obtained in practically quantitative yield, separates from boiling benzene in fine, pale yellow needles, melting at 163–164°.

Anal. Subs. 0.1554; CO_2, 0.2052; H_2O, 0.0380. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 36.01; H, 2.66.

The methyl ester was obtained in small quantity when the acid was treated with a saturated solution of hydrogen chloride in methyl alcohol but about one-half of the acid was recovered unchanged. A quantitative yield of the ester separated from the ethereal solution in lustrous, pure white needles when the acid was treated with diazomethane. It crystallizes from a small volume of methyl alcohol in fine, soft needles melting at 94°.

Anal. Subs. 0.1488; CO_2, 0.2079; H_2O, 0.0427. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 38.10; H, 3.19.

α-Bromo-5-bromo-2-methoxycinnamic Acid,



$$\left.\begin{matrix}(2)\mathrm{CH_3O}\\(5)\mathrm{Br}\end{matrix}\right>\mathrm{C_6H_3CH{=}CBrCOOH}$$

(221").——This acid separated slowly from the benzene filtrates of the yellow acid (163–164°) just described. After repeated crystallization from benzene it was obtained in the form of fine, pure white needles melting at 221°. The high-melting point led to the belief that the substance might be a polymer of the acid (163–164") formed by the action of light on the benzene solution of the latter. A molecular weight determination, however, and the fact that the substance readily decolorizes a solution of potassium permanganate in the cold to form 2-methoxy-5-bromobenzoic acid proved it to be an isomeric, not a polymeric, form of that acid.

Anal. Subs. 2.692 mg ; CO_2, 3.560 mg.; H_2O, 0.540 mg. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.71; H, 2.38. Found: C, 36.07; H, 2.24. Mol. wt. (Rast method). Subs. 0.570 mg.: camphor, 7.596 mg. *At* 9°. Calcd.: 336. Found: 333.5.

It was found possible to prepare this acid in quantity by exposing a saturated benzene solution of the yellow acid (163–164°) to bright sunlight. The first crystals to separate on spontaneous evaporation of the benzene, after two or three days' exposure, were those of the high-melting, colorless acid which is considerably less soluble in benzene than its isomer. By repeated exposures good yields of the acid (221°) were obtained.

The methyl ester of the acid (221°) may be formed in quantitative yield by the reaction of methyl alcohol saturated with hydrogen chloride or by diazomethane. It separates from methyl alcohol in firm, stiff needles, melting at 106–107°.

Anal. Subs. 0.1342; CO_2, 0.1856; H_2O, 0.0364. Calcd. for $C_{11}H_{10}O_3Br_2$: C, 37.71; H, 2.85. Found: C, 37.71; H, 3.01.

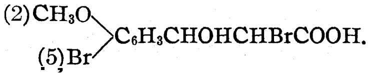
By treatment of both the acids (163–164°) and (221°) with a boiling 10% aqueous solution of potassium hydroxide a molecule of hydrogen bromide was readilv eliminated from each and 5-bromo-2-methoxyphenylpropiolic acid formed; it was crystallized from boiling benzene. The substance turns bright yellow and effervesces violently at 174°; it is evidently Perkin's acetylenic acid "melting with decomposition at about 168°."

Anal. Subs. 0.1244; CO_2, 0.2134; H_2O, 0.0317. Calcd. for $C_{10}H_7O_3Br$: C, 47.06; H, 2.74. Found: C, 46.98; H, 2.83.

Reaction of Water on the Two Dibromo Acids

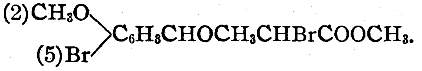
α-Bromo-β-hydroxy-*o*-methoxyhydrocinnamic Acid, $2\text{-}CH_3OC_6H_4CHOHCHBrCOOH$ (134°).—Biilmann prepared this hydroxy acid by shaking the high-melting dibromo acid with water. The low-melting dibromo acid (134°) gives the same substance under the same treatment.

By reaction of the hydroxy acid with an aqueous bromine solution Biilmann prepared α-bromo-β-hydroxy-5-bromo-2-methoxyhydrocinnamic acid,



$$\begin{matrix}(2)CH_3O\\(5)Br\end{matrix}\!\!>C_6H_3CHOHCHBrCOOH.$$

The acid melted at 137°, solidified and melted again at 154°. This behavior and especially the fact that after he had prepared the 154" substance he was not able to obtain the compound (137') in the same laboratory led Biilmann to conclude that the acids were dimorphic not isomeric. The behavior of the compound (137°) on melting is so like that of our dibromo acid (134") that the question of possible isomerism in the case of the two hydroxy acids arose. To test the point we have prepared the two hydroxy acids and treated both with an ethereal solution of diazomethane. From both solutions an oil separated which solidified completely. The solid, in each case, was crystallized from boiling ligroin from which it separated in firm clumps of crystals melting at 93–95°. A mixed melting point determination showed that the two were identical. The substance is the methyl ester of α-bromo-β-methoxy-5-bromo-2-methoxyhydrocinnamic acid



$$\begin{matrix}(2)CH_3O\\(5)Br\end{matrix}\!\!>C_6H_3CHOCH_3CHBrCOOCH_3.$$

Anal. Subs. 0.1559; CO_2, 0.2131; H_2O, 0.0517. Calcd. for $C_{12}H_{14}O_4Br_2$: C, 37.69; H, 3.66. Found: C, 37.29; H, 3.71.

The formation of the same compound by the action of diazomethane on the two hydroxy acids is an argument for their dimorphism rather than isomerism.

Reaction of Methyl Alcohol on the Two Dibromo Acids

α-Bromo-β-methoxy-2-methoxyhydrocinnamic Acid, $2\text{-}CH_3OC_6H_4CHOCH_3CHBrCOOH$ (118°).—Werner[7] prepared the methyl ester (m. p. 64") of this acid by warming the impure high-melting dibromo acid with methyl alcohol and hydrogen chloride; on hydrolysis of this ester the acid (m. p. 118") was obtained. We have prepared this acid, in good yield, by shaking the pure dibromo acid (177°) with an excess of cold methyl alcohol for nine hours.

α-Bromo-β-methoxy-2-methoxyhydrocinnamic Acid (136') .—On repeating Werner's experiment we obtained not only the acid described by him, melting at 118°, but in very small quantity an isomeric acid melting at 136°. The ester (64") formed by the action of methyl alcohol saturated with hydrogen chloride on the high-melting dibromo acid gives, on hydrolysis with alcoholic potassium hydroxide, a heavy deposit of the potassium salt of the acid (118"). On acidifying the alkaline filtrate from the separation of the potassium salt, a small amount of an acid separates slowly in fine, shining needles melting, after recrystallization from water, at 136". Analysis proves it to be isomeric with Werner's acid (118°).

Anal. Subs., 5.207 mg.: CO_2, 8.680 mg.; H_2O, 2.160 mg. Calcd. for $C_{11}H_{13}O_4Br$ C, 45.67; H, 4.53. Found: C, 45.46; H, 4.64.

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[7] Werner, *Ber.,* 39, 27 (1906).

When the low-melting dibromo acid (134°) was shaken with an excess of cold methyl alcohol, this methoxy acid (136°) was the sole product of the reaction.

Summary

Two isomeric dibromo acids have been prepared in the pure condition by the action of bromine on methylcoumaric and on methylcoumarinic acids.

The reactions of these acids with potassium hydroxide, water, an aqueous solution of bromine and methyl alcohol have been studied.

NEW YORK, N. Y.

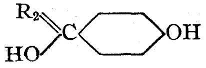
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS

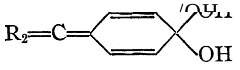
BY L. C. ANDERSON AND M. GOMBERG

RECEIVED SEPTEMBER 30, 1927 PUBLISHED JANUARY 5, 1928

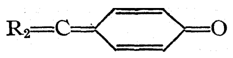
It has been shown[1] that when p-hydroxytriphenylcarbinol is crystallized from 50% acetic acid, the product obtained is yellow in color, melts at 139–140°, and when warmed it loses a molecule of water in a comparatively short time, forming fuchsone (III). On the other hand, when this carbinol is crystallized from alcohol containing a trace of ammonia, it is obtained colorless, melts at 157–159°, and when warmed loses a molecule of water at a very slow rate, fuchsone being the product. It has been demonstrated that neither of the modifications contains water of crystallization and that they are not simply two different crystalline forms of the same material. One modification can be changed into the other by the proper choice of solvent; heat or light favors the colored form. Structures (I) and (II) have been assigned to these forms:



I. Benzenoid (colorless)



II. Quinonoid (colored)



III. Fuchsone

It has been our purpose to study these tautomeric forms by means of the quantitative absorption spectra of their solutions. The present paper deals with p-hydroxytriphenylcarbinol and with o-cresyldiphenylcarbinol (3-methyl-4-hydroxytriphenylcarbinol). Work on other carbinols will appear in subsequent papers.

Procedure.—For the measurement of absorption spectra in the ultraviolet, we used a Judd-Lewis sector photometer (Hilger)[2] and a Hilger quartz spectrograph, Size C. The source of light was a condensed spark between tungsten electrodes under distilled water and, when photo-

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[1] (a) Gomberg, THIS JOURNAL, 35, 1035 (1913); (b) Gomberg and co-workers, 37, 2575 (1915); (c) 38, 1577 (1916); (d) 39, 1674 (1917); (e) 39, 2392 (1917); (f) 42, 1864 (1920); (g) 42, 1879 (1920); (h) 45, 190 (1923); (i) 47, 2392 (1925).

[2] Adam Hilger, Ltd., London, Catalog No. H-40.

graphed through the photometer, its spectrum was continuous and intense to a frequency of about 4350. The electrical set-up was patterned after the one used for similar purposes at the Bureau of Standards[3] Some of the curves where absorption was in the visible region of the spectrum were checked by the use of a Nutting photometer and Hilger wave-length spectrometer with a Pointolite lamp as the source of light.

About 0.1 g. of the material under investigation was weighed into a 25 or 50cc. volumetric flask and the flask filled with the solvent. A one centimeter absorption tube filled with this solution was inserted in one section of the photometer and a similar tube filled with the solvent was placed in the other. The sector in the beam of light passing through the solvent was set at extinction coefficient values of 0.1, 0.2, etc., up to 1.2 and the two spectra were photographed at each setting. Five cc. of the solution was then diluted to 25 cc. and a new series of exposures taken on another plate. Further dilutions were made until the peaks of the absorption bands had been photographed. When this procedure is followed, the first one or two exposures taken of a diluted solution coincides with the last exposures taken of the solution before diluting. The overlapping sections of the curves assisted us materially in checking our dilutions and in obtaining continuous curves. At least two and sometimes six or seven samples of a substance have been used before a quantitative absorption curve was considered to have been obtained.

The points at which the comparison beam and the beam which had passed through the solution were of equal intensity were determined under a low power lens in a comparator similar to the one used at the Bureau of Standards. The scale of the comparator was fitted with a vernier reading to a tenth of a millimeter. A curve showing the relationship between the comparator readings and frequencies was made by means of the spectrum of the copper spark.

As regards the choice of suitable solvents, very few are transparent to the shorter ultraviolet rays. Of these methyl alcohol and ethyl alcohol, although transparent, are of necessity eliminated, since in solutions of the hydroxytriarylcarbinols in alcohols, an equilibrium is established between the two tautomers.[4] Water cannot be used for two reasons: first, the insolubility of the carbinols in it and, second, the possibility of its reaction with the solutes. Ether has been found very satisfactory and, in every case studied thus far, the absorption spectrum of the ether solution that has been standing for several weeks has been found to be identical with that of the fresh solution.

Purification of Materials.—The compounds discussed in this paper were purified until their quantitative absorption spectra remained constant.

p-Hydroxytriphenylmethane[5] obtained from the carbinol by reduction with zinc dust and acetic acid was recrystallized from ether; m. p. 110°.

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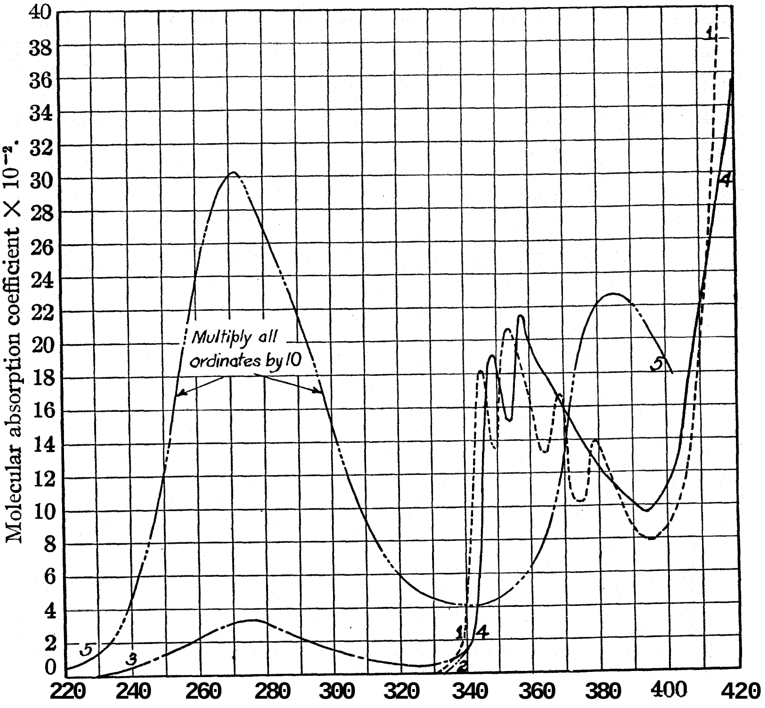
[3] Bureau of Standards Scientific Paper No. 440, June, 1922.

[4] (a) Ref. 1a, p. 1037; (b) Omdorff, Gibbs, McNulty and Shapiro, THIS JOURNAL. 49, 1545 (1927).

[5] Bistrzycki and Herbst, *Ber.*, 35, 3137 (1902).

p-Hydroxytriphenylcarbinol, benzenoid tautomer, was recrystallized three times from alcohol containing a trace of ammonia. It was filtered in an atmosphere which was free from acid fumes and the substance dried over soda lime. The crystals acquired a very pale greenish-yellow color; m. p. 159–160°.

p-Hydroxytriphenylcarbinol, quinonoid tautomer, was recrystallized from water solutions of acetic acid containing 50, 60 and 70% of acid, and from solutions containing 50 and 60% of propionic acid. The crystals were allowed to stand in contact with the mother liquor for from twenty-four to forty-eight hours and were washed on the filter plate with a small quantity of solvent. They were dried to constant weight in a desiccator which contained a saturated solution of potassium hydroxide and in which the pressure was reduced to 3–4 mm.; m. p. 139–140°.



1. ----Methane. 2. ———Benzenoid form of the carbinol. 3. ———Quinonoid form of the carbinol. 4. ————Both forms—benzenoid and quinonoid carbinols. 5. —————Fuchsone of the carbinol.

Fig. 1.—*p*-Hydroxytriphenylmethane and its derivatives.

Diphenylquinomethane, or the fuchsone of *p*-hydroxytriphenylcarbinol, was obtained by the dehydration of the carbinol. It was recrystallized twice from ether; m. p. 168'.

3-Methyl-4-hydroxytriphenylmethane[6] was prepared by reducing *o*-cresyldiphenylcarbinol with zinc dust and acetic acid. It was recrystallized from ether; m. p. 100°.

3-Methyl-4-hydroxytriphenylcarbinol, benzenoid tautomer, was obtained when

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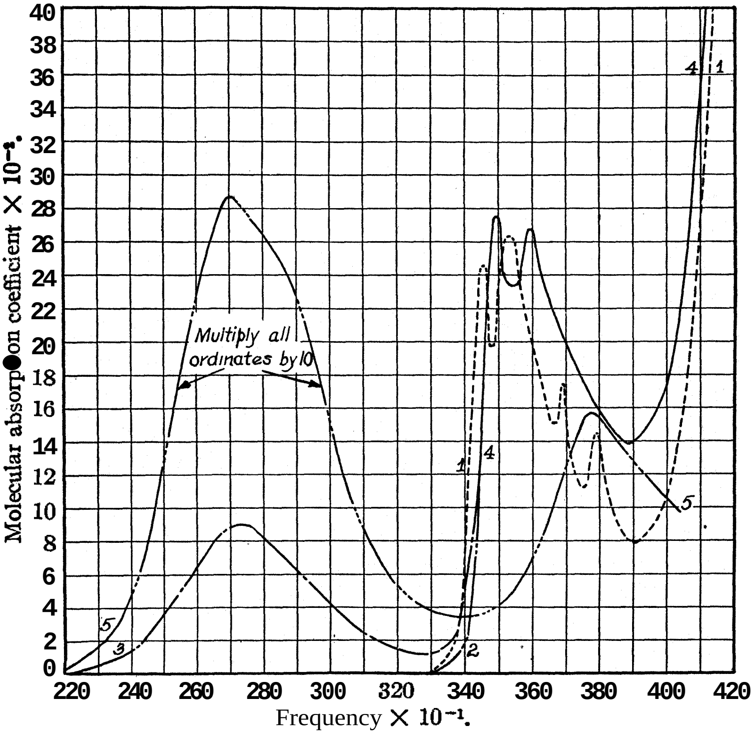
[6] Bistrzycki and Zurbriggen, *Ber.* 36, 3561 (1903).

carbon dioxide was passed into an alkaline solution of the fuchsone. The colorless crystals were recrystallized from ether; m. p. 151°.

3-Methyl-4-hydroxytriphenylcarbinol, quinonoid tautomer, was obtained when either the colorless modification of the carbinol, or the corresponding fuchsone, was crystallized from 50, 60 or 70% aqueous solutions of acetic acid, or 50 or 60% aqueous solutions of propionic acid. The crystals were washed with pure solvent and dried in an evacuated desiccator containing soda lime. The literature[7] records 108–109° as the melting point of this modification. All samples prepared by us melted at 138–139°. The color of the crystals obtained varied with the acid concentration but by means of quantitative absorption spectra we have been able to show that this difference in color is due to the size of the crystals; the finely divided material from the 50% acetic acid solution having a lighter yellow and the larger crystals from the 70% acid having a deeper yellow color than the material from the 60% acid; a similar relationship held true for the material crystallized from the propionic acid solutions. Ether solutions of all these samples, however, have identical quantitative absorption spectra.



1. - - - - -Methane. 2. — - - —Benzenoid form of the carbinol. 3. — - —Quinonoid form of the carbinol. 4. ———Both forms—benzenoid and quinonoid carbinols. 5. — - - - —Fuchsone of the carbinol.

Fig. 2.—*o*-Cresyldiphenylmethane and its derivatives.

3-Methyl-4-hydroxyquinodiphenylmethane was prepared by heating *o*-cresyldi-

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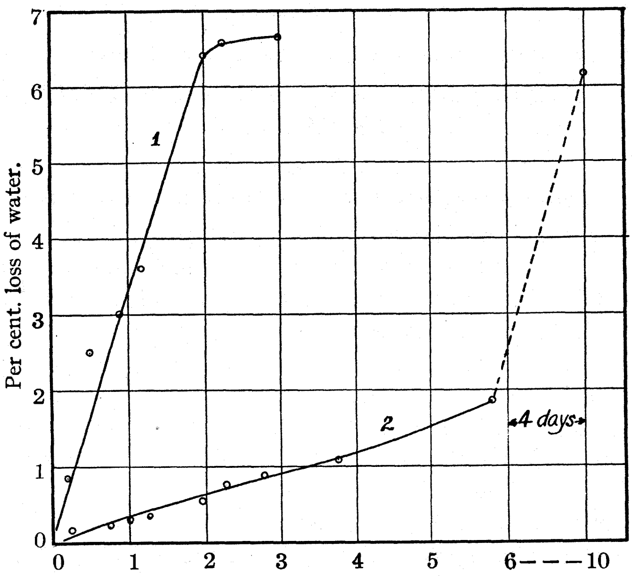
[7] Ref. 1c, p. 1585; ref. 6, p. 3558.

phenylcarbinol at 75° until it had reached constant weight. It was crystallized from ether; m. p. 176°.

Further proof has been obtained that the quinonoid modification of o-cresyldiphenylcarbinol is not a mixture of the benzenoid form and the fuchsone. By the application of Beer's law we calculated that the intensity of the absorption band of the quinonoid form of o-cresyldiphenylcarbinol at frequency 2730 is equal to that of a mixture composed of 3.17% of fuchsone and 96.83% of the benzenoid form. Mixtures of approximately this composition were made and the absorption spectrum of these mixtures was found to be very similar to that of the quinonoid carbinol. When the melting point of this mixture was determined, however, it was observed that the mixture began to soften several degrees below the temperature at which it melted, whereas the melting point of the quinonoid modification is always quite sharp. Moreover, the mixture made by us loses water when placed in a current of warm air at a rate quite different from the rate of loss by the true quinonoid carbinol (Diagram I).



Time in days. Temp. = 75°.

Curve 1 = Quinoid form of *o*-cresyldiphenylcarbinol.
Curve 2 = 3.16% of fuchsone + 96.84% of benzenoid form of *o*-cresyldiphenylcarbinol.

Fig. 3.

We therefore conclude that within a fairly wide range of acid concentration only a single product, namely, the quinonoid tautomer, is formed when either the *p*-hydroxytriphenylcarbinol or *o*-cresyldiphenylcarbinol is recrystallized from dilute acetic or propionic acid.

Summary

The quantitative absorption curves of ether solutions of the methane, the benzenoid carbinol, the quinonoid carbinol and the fuchsone of each—the *p*-hydroxytriphenylcarbinol and o-cresyldiphenylcarbinol—have been carefully determined. The spectroscopic results constitute further evidence that *p*-hydroxytriphenylcarbinol and *o*-cresyldiphenylcarbinol exist each in two tautomeric forms, a quinonoid and a benzenoid,

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ABSORPTION SPECTRA OF SOME TRIPHENYLMETHANE DERIVATIVES

BY L. C. ANDERSON

RECEIVED SEPTEMBER 30, 1927 PUBLISHED JANUARY 5, 1928

The curves which we have obtained for the quantitative absorption of ultraviolet light by solutions of triphenylmethane and some of its derivatives differ in many respects from those which other investigators have recorded. These differences are due partly to variations in equipment and procedures used at different laboratories but partly, however, to the fact that in some of the recently published work no account was taken of the fact that reaction between the solute and the solvent had given rise to compounds which differed from the original solute and which consequently possessed different absorption spectra.

As previously mentioned,[1] we have found ether to be a very satisfactory solvent to use in this type of work. We have examined layers of pure ethyl ether as thick as two centimeters and in no case has the pure liquid shown selective absorption[2] in the spectrum included by our equipment,[1] which allows measurements to be made at frequencies from 4550 mm.^{-1} to the visible.

The ultraviolet absorption spectra of solutions of triphenylmethane and triphenylcarbinol have been described by Hartley,[3] Baker[4] and Hantzsch[5] who give curves which show absorption only in broad bands. Orndorff, Gibbs, McNulty and Shapiro[6] have given curves which show the quantitative absorption of ultraviolet light by absolute ethyl alcohol solutions of these compounds. They report ten peaks for the solution of triphenylmethane and seven for triphenylcarbinol between 3700 and

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[1] Anderson and Gomberg, THIS JOURNAL, 50, 203 (1928).

[2] See for discussion, Smith, Boord, Adams, and Pease, THIS JOURNAL, 49, 1335 (1927); De Laszlo, *ibid.*, 49, 2106 (1927).

[3] Hartley, *J. Chem. Soc.*, 51, 152 (1887).

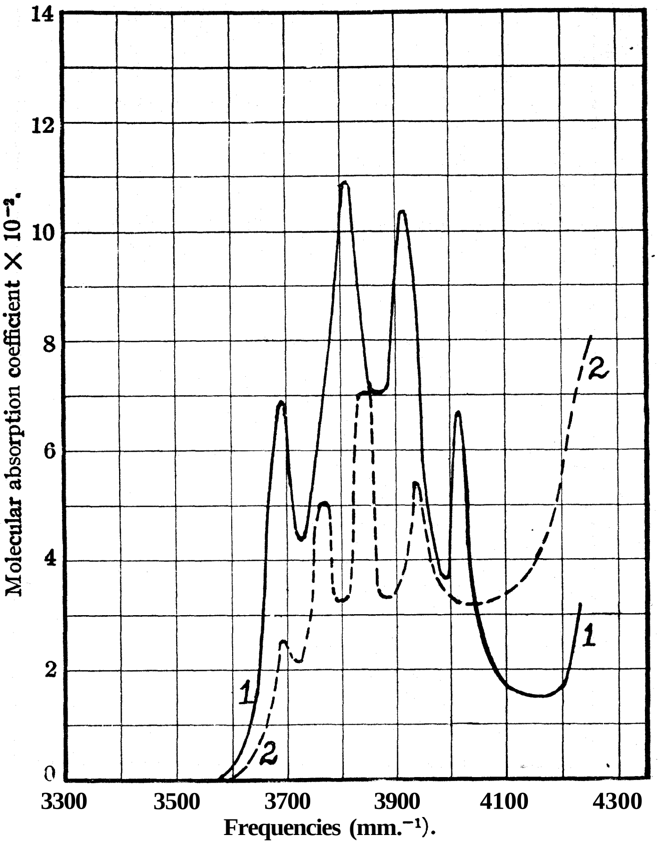
[4] Baker, *ibid.*, 91, 1490 (1907).

[5] Hantzsch, *Ber.*, 52, 509 (1919).

[6] Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, 49, 1541 (1927).

4200 mm^{-1}. Using ether solutions we have located only the four prominent peaks of each compound between the above frequencies. A careful examination of our plates has not given any indication of several of the absorption peaks which the latter investigators have found in alcohol solutions.

The quantitative absorption spectra of solutions of the ethyl ether of triphenylcarbinol, whether in ethyl ether or absolute ethyl alcohol, differ only in intensity; the position of the bands at frequencies 3690, 3760, 3840 and 3930 are virtually unchanged by the change of solvent.



1. ——— = Triphenylmethane; 2. ---- = Triphenylcarbinol.

Fig. 1.

It is known that triphenylchloromethane reacts with hot ethyl alcohol to form the ethyl ether of triphenylcarbinol,[7] and we have found that even in the cold the conversion of the chloride to the ether by alcohol is almost

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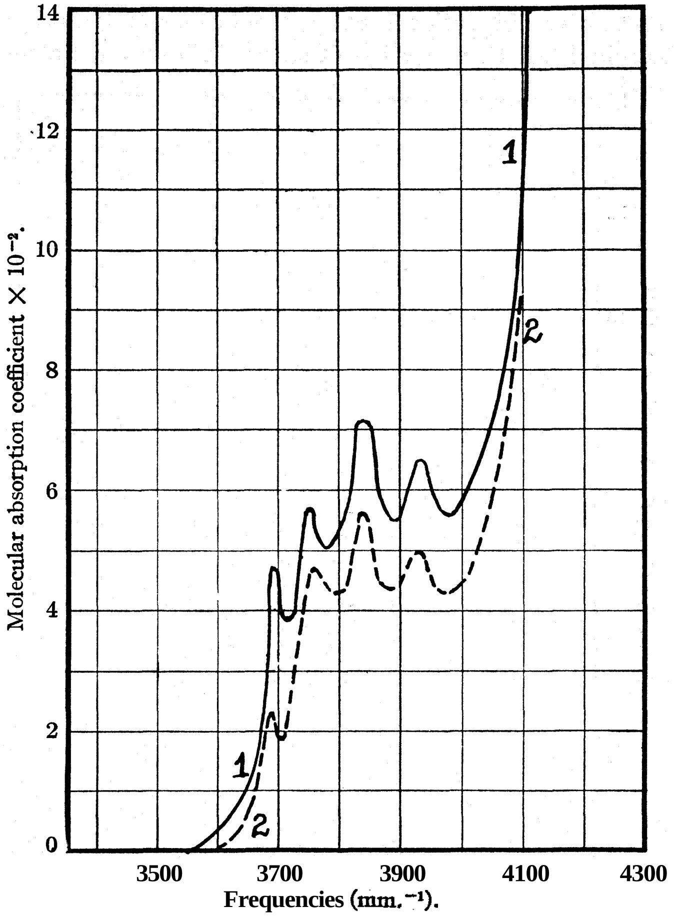
[7] (a) Hemilian, Ber., 7, 1208 (1874); (b) Friedel and Crafts, Ann. *chim., phys.* [6] 1, 502 (1884); (c) Frey, Bar., 28, 2518 (1895).

quantitative. A solution of triphenylchloromethane in ether has absorption bands at frequencies 3660, 3740, 3830 and 3920 mm^{-1}. When, however, the chloride is dissolved in absolute ethyl alcohol (neutral), the frequencies of the absorption peaks become practically identical with those of the pure ethyl ether of triphenylcarbinol, there being only a slight difference in the intensity of the peaks. We conclude that the quantitative absorption curve of a solution of triphenylchloromethane in absolute ethyl alcohol as described by Orndorff, Gibbs, McNulty and Shapiro is not due to triphenylchloromethane but is due to the ethyl ether of triphenylcarbinol.

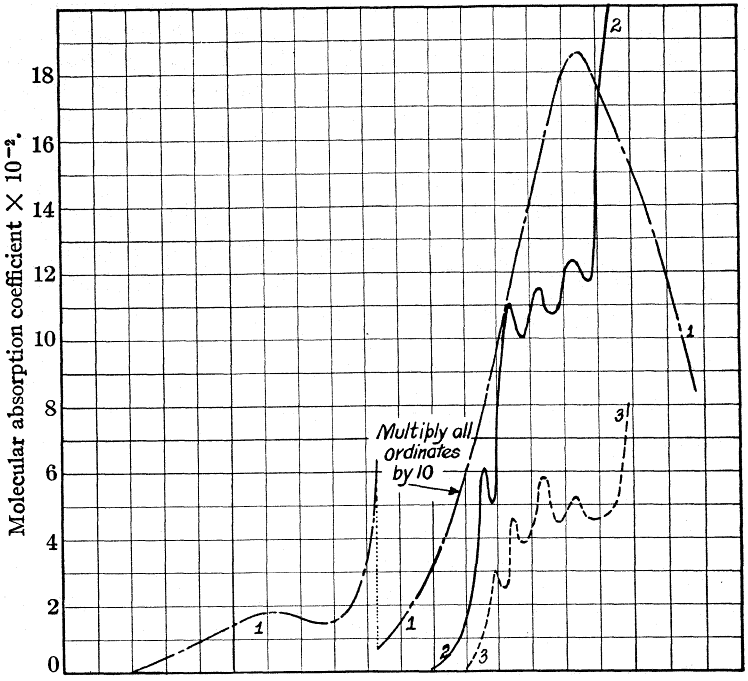


1. ——— = Solution in ether; 2. ‐ ‐ ‐ ‐ = Solution in neutral absolute ethyl alcohol.

Fig. 2.—Ethyl ether of triphenylcarbinol.

Purification of Compounds.—Benzophenone was distilled under reduced pressure and, after three repeated crystallizations from alcohol, it was recrystallized from ether; m. p. 47°. It was used by us to check our curves with data that have been given in the literature. Our results agree very well with those of the most recent investigator.[8]

Triphenylmethane was prepared by the reduction of triphenylcarbinol with zinc dust and acetic acid. It was recrystallized from benzene and then twice from ether; m. p. 92°.



1. — - — = Benzophenone in alcohol; 2. ——— = Triphenylchloromethane in ether; 3. - - - - = Solution obtained by dissolving triphenylchloromethane in neutral absolute ethyl alcohol.

Fig. 3.

Triphenylcarbinol, made from bmzophenone by the Grignard reaction with phenylmagnesium bromide, was recrystallized once from benzene and then twice from ether; m. p. 162°.

Triphenylchloromethane was made by the reaction between a benzene solution of triphenylcarbinol and dry hydrogen chloride in the presence of anhydrous calcium chloride. It was recrystallized from absolute ether just prior to being used; m. p. 111–112".

The ethyl ether of triphenylcarbinol was prepared by adding pure triphenylchloromethane to an alcohol solution of sodium ethylate. After it was crystallized twice from ether, it melted at 83°. The ethoxy compound was also made by allowing a solu-

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[8] Scheibe. *Ber.*, 59, 2626 (1926).

tion of pure triphenylchloromethane in neutral absolute ethyl alcohol to stand at room temperature overnight. The solvent was evaporated under reduced pressure in a desiccator which contained fused calcium chloride. Samples of the dried residue melted at 81–82° and the melting point of mixtures of this residue and the purified ether, which was prepared as first described, showed that the residue was practically pure ethyl ether of triphenylcarbinol.

The absolute ethyl alcohol which was used as solvent was obtained by a careful fractionation of 99.5% ethyl alcohol which had been distilled from anhydrous potassium hydroxide. A two centimeter layer of the liquid was perfectly transparent at all frequencies within the limit of our equipment. The ether that was used as solvent was in most cases a product obtained on the market as "Reagent Ether Anhydrous." This ether, without further purification, was optically clear and was without effect upon the solute; however, for some of the work, it was distilled from fresh metallic sodium.

Summary

1. Curves are presented which show the quantitative absorption spectra in the ultraviolet of ether solutions of triphenylmethane, triphenylcarbinol, triphenylchloromethane and the ethyl ether of triphenylcarbinol; also curves which show the absorption of absolute ethyl alcohol solutions of benzophenone and the ethyl ether of triphenylcarbinol.

2. It has been shown that the curve obtained from a solution of triphenylchloromomethane in neutral absolute ethyl alcohol is in reality the absorption curve of the alcohol solution of the ethyl ether of triphenylcarbinol.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE REACTION OF ISOPROPYL IODIDE WITH MERCURIC CHLORIDE

BY BEN H. NICOLET AND WILLIAM McDANIEL POTTS[1]

RECEIVED SEPTEMBER 30, 1927 PUBLISHED JANUARY 5, 1928

Conant and others[2] have recently studied the reaction RCl + KI = RI + KCl (R representing a considerable variety of alkyl and other radicals) in some detail. With the simpler alkyl chlorides, it took place some 60 times more rapidly for primary than for secondary chlorides. They found the reaction quite strictly of the second order, and so slightly reversible that the opposing reaction (if any) did not need to be considered in the calculation of velocity constants.

Nevertheless, Oppenheim[3] in 1860 reported that ethyl chloride and amyl chloride could be obtained by the action of mercuric chloride on the

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[1] The material here presented was used by William McDaniel Potts in partial satisfaction of the requirements for the degree of Master of Science, at the University of Chicago, 1927.

[2] (a) Conant and Kirner, THIS JOURNAL, **46**, 352 (1924); (b) Conant and Hussey, *ibid.*, **47**, 476 (1925); (c) Conant, Kier and Hussey, *ibid.*, **47**, 488 (1925).

[3] Oppenheim. *Ann.*, **140**, 207 (1860).

respective iodides. By a similar process, Maumene[4] made $ClCH_2CH_2I$ and $C_2H_4Cl_2$ from $C_2H_4I_2$. Later, Linnemann[5] prepared butyl chloride in 70% yield by the action of mercuric chloride on butyl iodide at 120–130°.

This reaction[6] thus has the appearance of being an effective reversal of the conversion of chlorides to iodides as studied by Conant and his collaborators. Such a reversal might be explained as due to the fact that the concentration of iodide ion in mercuric iodide solutions is excessively small, even in comparison with the chloride-ion concentration in solutions of mercuric chloride.

On the grounds suggested, the reaction of isopropyl iodide with mercuric chloride in dry ether was studied, and found to take place at a rate proportional to the concentrations of these two substances, and also to the concentration of the mercuric iodide. In the calculation of velocity constants, it was found possible to neglect the reverse reaction. *Iso*propyl iodide was chosen after it had been found that n-propyl iodide reacted at least 50 times more slowly. This ratio again favors the idea that the reaction is really a reversal of that studied by Gonant.

Experimental Part

Choice of a Solvent.—It has already been shown[7] that alcohol is not a suitable solvent for the study contemplated, as in it the chief reaction would be one of alcoholysis, catalyzed by the mercuric halide. A suitable solvent would be one which did not react with mercuric salts, which contained no hydroxyl group and which dissolved mercuric iodide to a considerable extent. As the simplest compromise, absolute ether was selected, although it dissolved so little mercuric iodide that, at convenient concentrations of the reacting substances, it was possible to follow the reaction only to 25–50% completion; beyond this, mercuric iodide separated.

Procedure.—The reacting substances were dissolved in absolute ether in the desired proportions, the solution was made up to 200 cc. and the whole kept in a thermostat at 25°. Samples of 10 cc. were withdrawn at suitable intervals and analyzed for inorganic iodine as follows:

The sample was placed in a 150cc. flask and dry air drawn through until the ether and organic iodide were completely evaporated. Blank determinations showed that less than 0.5% of the organically combined iodine was converted to mercuric iodide under these conditions. The dry residue was covered with water, made acid with sul-

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[4] Maumene, *Jahresb. über die Fortschritte der Chem.*, 1869, p. 345.

[5] Linnemann, *Ann.*, 161, 197 (1872).

[6] We have also found that when solid mercuric chloride is covered with a moderate excess of ethyl iodide in a closed flask, which is allowed to stand for some days, remarkably good crystals of mercuric iodide separate. This is, in fact, an excellent method of growing such crystals. It might be predicted that isopropyl iodide would give more rapid results, but it is not clear whether this would be an advantage in the formation of such crystals.

[7] Nicolet and Stevens, THIS JOURNAL, 50, 135 (1928).

furic acid and mossy zinc added. The solution was allowed to stand until the mercury was completely precipitated. The iodine was then liberated with nitrosylsulfuric acid, extracted with carbon disulfide, and the extract titrated with standard thiosulfate solution.

Typical results are given in Table I. At all the concentrations listed, mercuric iodide was still completely dissolved. Each run was discontinued when the iodide began to separate.

TABLE I

REACTION OF MERCURIC CHLORIDE WITH *ISO*PROPYL IODIDE IN ETHER AT 25°

Expt. no.	Time, hrs.	*Iso*propyl iodide transformed, moles	K
Case A: Mercuric chloride, 0.1425 *M*; *iso*propyl iodide, 0.285 M			
1	70	0.0194	
			0.56[a]
2	118	.0305	
			.57
3	169	.0475	
			.58
4	215	.0668	
		Av.	.57
Case B: Mercuric chloride, 0.1425 M; *iso*propyl iodide 0.1425 M			
1	92	0.0113	
			0.77[b]
2	236	.0283	
			.68
3	308	.0395	
			.83
4	355	.0497	
			.70
5	404	.0592	
			.82
6	452	.0700	
		Av.	.76
Case C: Mercuric chloride, 0.0712 *M*; isopropyl iodide, 0.1425 *M*; mercuric iodide (initial), 0.0185 M			
1	19	0.00162	0.45[c]
2	93	.0064	.35
3	141	.0107	.38
4	187	.0157	.41
5	284	.0276	.47
6	309	.0299	.47
		Av.	.44

[a] Values for Case A calcd. for successive intervals from Equation 2.

[b] Values for Case B calcd. for successive intervals from Equation 1.

[c] Values for Case C calcd. from Equation 3.

Calculation of Velocity Constants

The reaction is obviously autocatalytic. In the equation

$$\underset{(a)}{HgCl_2} + \underset{(b)}{2(CH_3)_2CHI} = \underset{(d)}{HgI_2} + 2(CH_3)_2CHCl$$

the initial concentration of each substance present may be represented by the letter beneath its formula. The values of K in Table I were calculated, for Case B, from the formula

$$\frac{dx}{dt} = \frac{K}{4}(2a - x)\,(b - x)x \qquad (1)$$

It is apparent that, at the time t, the concentrations of mercuric chloride and iodide may be represented by $(2a - x)/2$ and $x/2$, respectively, x representing moles of iodide transformed. For Case A (in which $2a = b$), this becomes

$$\frac{dx}{dt} = \frac{K}{4}(b - x)^2x \qquad (2)$$

Finally, in Case C, mercuric iodide was added at the beginning to confirm the assumption that it was responsible for the catalytic effect observed. As for simplicity concentrations were so chosen that $2a = b$, the corresponding equation was

$$\frac{dx}{dt} = \frac{K}{[illegible]}(b - [illegible])\,[illegible]\,(d\ x) \qquad (3)$$

A possible interpretation of the reaction mechanism which would be consistent with the equations used would be the following. Isopropyl iodide reacts extremely slowly with mercuric chloride, but with mercuric iodide it forms a complex $(CH_3)_2CHI{\cdot}HgI_2$ which reacts (in the molecular ratio 1:1) with mercuric chloride (or perhaps with chloride ion) at a considerably greater rate. This complex is relatively rapidly formed in reversible reaction, so that its concentration (probably small) is proportional to $x(b - x)/2$.

Discussion of Results

In Cases A and B, the nature of the integrated equation requires that the constants be calculated between intervals and not from zero time. To save space in presentation, these calculations have been made between successive intervals, which magnifies the errors of individual determinations. The values of K are, however, sufficiently consistent in each series to indicate agreement with the type of equation used. The variation in the average values for the different series still requires explanation.

While the data presented give a fairly satisfactory account of the reaction under discussion, there is a definite logical defect in the equations used in the calculations given. It is not strictly possible that the entire reaction velocity should be proportional to the concentration of a product of the reaction not initially present.

It must be assumed, therefore, that the observed velocity is really made up of the sum of the velocity represented in accordance with the equations used and the velocity of the (evidently much slower) reaction of isopropyl iodide with mercuric chloride alone. Using the same symbols as before, the true equation would probably have one of the following forms

$$\frac{dx}{dt} = \frac{K}{4}(2a - x)(b - x)x + \frac{K'}{2}(2a - x)(b - x) \tag{4}$$

$$\frac{dx}{dt} = \frac{K}{4}(2a - x)(b - x)x + \frac{K'}{4}(2a - x)^2(b - x) \tag{5}$$

In Equation 4, the slow reaction is represented as being the simplest possible. Equation 5 represents the assumption that the slow reaction is catalyzed by mercuric chloride in the same way that the main reaction is catalyzed by mercuric iodide.

Calculations of constants based on both these equations have been made but, as might have been expected from the figures already presented, the "slow component" of the reaction is so very slow, and makes such a slight contribution to the total "K," that a decision between the mechanisms suggested in these two equations would be quite impossible with the present data.

Further work is planned to determine more definitely whether the present reaction actually constitutes a true reversal of the reaction studied by Conant. If it does, there is every reason to believe that the latter reaction should also be powerfully catalyzed by mercuric iodide. It is apparent that this test cannot be applied experimentally, since the catalyst (HgI_2) is incompatible with one of the reactants (iodide ion). While obviously no contradiction is here involved, the apparent paradox is interesting.

Summary

1. The reaction of isopropyl iodide (and presumably of other iodides) with mercuric chloride (measured in ether at 25°) takes place at a rate proportional to the product of the concentrations of these two substances and of the mercuric iodide formed. The reaction evidently goes practically to completion.

2. This reaction is pictured as a reversal of that of alkyl (and other) chlorides with iodide ion. which also goes practically to completion.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM CENTRAL ILLINOIS TESTING LABORATORIES]

DIRECT NESSLERIZATION OF KJELDAHL DIGESTIONS

BY H. M. CHILES

RECEIVED OCTOBER 4, 1927 PUBLISHED JANUARY 5, 1928

The method outlined here is the outgrowth of a study started in the summer of 1922 as one step in the simplification of the methods of Folin-Wu and of Benedict for blood analysis to make them more suitable as routine tests for use by technicians of limited basic training. The work was started in the pathological laboratory of the St. John's Hospital, Springfield, Illinois, and continued at the present location since that time.

The Nesslerization of ammonia in the presence of considerable quantities of inorganic salts is an old problem. The published methods to date seem to be confined to limiting the amount or the nature of the salts present. It seems strange that so little apparent effort has been made to attack the problem by the use of protective colloids. Folin and Denis[1] have developed a method for the direct Nesslerization of micro Kjeldahl digestions by the substitution of phosphoric acid for a large part of the sulfuric acid and omitting the alkali sulfate generally used. This digestion mixture has the serious fault of attacking the glassware, leaving a considerable amount of insoluble sediment; moreover, only low concentrations of ammonia can be Nesslerized, limiting the method to micro determinations.

By the use of a protective colloid to prevent precipitation of the color in the Nesslerized solutions as here described it is possible to Nesslerize directly any of the commonly used Kjeldahl digestion mixtures. Moreover, it is thus possible to Nesslerize a much higher concentration of ammonia in the presence of relatively large amounts of alkali sulfates than by the usual methods even in the absence of any extraneous salts. A number of colloids have been tried for this purpose but by far the most satisfactory one found to date is a specially prepared gum arabic solution. By the use of this material it is possible to successfully Nesslerize concentrations of ammonia as high as 20 mg. of nitrogen per 100 cc. of final solution and this in the presence of from 5 to 8 g. of anhydrous sodium or potassium sulfate. Such solutions develop their maximum color rapidly and do not start to precipitate for a considerable time; in fact, aliquot portions of Kjeldahl digestions containing in the Nesslerized solution 5 mg. of ammonia nitrogen per 100 cc. have been retained without noticeable precipitation for as long as two weeks. Satisfactory Nesslerizations have even been carried out in solutions saturated with sodium sulfate.

The method has been tried in comparison with the usual Kjeldahl methods both macro and micro on the following materials: blood, blood

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[1] Folin and Denis, *J. Biol. Chem.*, 26,473 (1916).

filtrates, urine, milk, grain feeds, tankage, and cottonseed meal. The following table shows some of the comparative results.

TABLE I

COMPARATIVE RESULTS

Sample	Distillation and titration	Direct Nesslerization	Aeration and Nesslerization
Blood	2.95	2.97	....
Blood	2.62	2.58	....
Urine	1.22	1.24	....
Urine	0.835	0.840	....
Milk	.634	.632	....
Breast milk	.227	.228	....
Breast milk	.218	.218	....
Blood N. P. N.	.0316	.0316	0.0310
Blood N. P. N.	.0298	.0299	.0297
Blood N. P. N.	.0424	.0426	.0420
Cottonseed meal	7.02	7.11, 6.94 **Av.** 7.05	....
Cottonseed meal	6.98	7.07, 6.90 **Av.** 7.03	....
Tankage	9.68	9.78, 9.56 **Av.** 9.69	....
Tankage	9.52	9.63, 9.44 **Av.** 9.55	....
Mixed dairy feed	1.69	1.70, 1.66 **Av.** 1 67	....

In the above comparative determinations, digestions were made in the usual manner, the digested solutions were made up to a definite volume and proper aliquots used for each method. In some of the digestions copper was used and in some mercury. For products of low nitrogen content the result is calculated from one careful reading at the colorimeter. For materials of high nitrogen content the result is calculated from the average of five distinct readings; the results calculated from the highest and the lowest readings are also reported. A study of the comparative results will show only the differences to be expected due to the inherent inaccuracy of colorimetric determinations.

Since one of the principal advantages of this method is the saving of time, we have found it expedient to use it in combination with the sulfuric-perchloric acid decomposition method of Mears and Hussey.[2] This we have found very satisfactory for many materials although the results are usually somewhat low for urine and for this reason we prefer to omit the perchloric acid in this case. For micro determinations we have found the following digesting mixture to be very convenient: concentrated sulfuric acid 70 cc., water 50 cc., 20% perchloric acid 20 cc., anhydrous sodium sulfate 15 g. and copper sulfate 1 g.

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[2] **Mears and Hussey, J.** *Ind. Eng. Cham.*, 13, **1054** (1921).

For micro analysis blood, urine, milk and similar liquid materials are suitably diluted and such aliquots as will normally give from 2 to 5 mg. of ammonia nitrogen are taken and digested with 1 or 2 cc. of the above digestion mixture in the usual manner, heating for at least two minutes after the solutions are colorless. If desired, particularly for urine, the perchloric acid may be omitted. The mixture after digestion is cooled, transferred to a volumetric flask and 5 cc. of colloid solution is then added for each 100 cc. of final volume; two or three drops of Nessler solution are added to serve as indicator and the solution neutralized with 10% sodium hydroxide solution. The solution is then diluted and the Nessler solution, to which the colloid has been added, is run in to the amount of from 10 to 25 cc., according to the nitrogen content of the solution, for each 100 cc. of final solution. No care need be taken as to the manner of addition of the Nessler solution except to note its volume, which must be the same as for the preparation of the standard for comparison. After the addition of the Nessler solution, the flask is filled to the mark, shaken and compared with Nesslerized standard prepared in the same manner.

For analysis of feeds and other dry materials it is best to make the usual macro digestion using either copper sulfate or mercury for catalyst. In general copper is preferable as it is easier to get crystal clear Nesslerization when it is used than in the case of mercury. When mercury is used as a catalyst somewhat more protective colloid should be added to the solution before neutralization; also the solution should be diluted as much as possible before neutralizing. The turbidity due to mercuric oxide formed in neutralizing when a slight excess of alkali is added usually, however, entirely clears after Nesslerization. By the use of the colloid as described it is possible to add the solution to be Nesslerized to the diluted Nessler and colloid solutions and in this way it is unnecessary to make several standards, as an acid mixture corresponding to the digested mixture may be neutralized and the Nessler solution added and then the standard ammonia solution until it approximately matches the unknown. It is, of course, very necessary to use an accurate buret for the measurement of the concentrated standard solution.

For routine work we have found it desirable to use definite amounts and dilutions and obtain results from a prepared chart referred to colorimeter scale readings.

Preparation of Protective Colloid Solution

While many samples of gum arabic may be used without special preparation, all samples which we have examined give considerable color with Nessler solution as well as an appreciable reduction to free mercury upon standing for some time. All of the ammonia and most of the other interfering substances can be easily removed by treatment of the solution with Permutit powder.

Ten grams of powdered gum arabic are slowly added with vigorous stirring to 190 cc. of ammonia-free water and the mixture stirred until the gum is entirely dispersed. The solution is transferred to a flask and approximately 4 g. of Permutit powder as prepared for ammonia determinations is added and the mixture shaken at intervals for ten minutes. Upon standing for a few minutes the Permutit powder settles and the slightly turbid supernatant liquid is decanted. This liquid should at most give only a faint coloration with Nessler solution; if a test portion gives an appreciable coloration with Nessler solution, the treatment with a fresh portion of Permutit powder is repeated. The solution as prepared is somewhat turbid but the insoluble material will settle out on standing for some hours. The turbidity in the freshly prepared solution, however, usually does not interfere and the solution may be used at once. Some samples of gum arabic treated as above have considerable reducing action on the Nessler solution; such solutions may be oxidized by the addition of small amounts of sodium peroxide, allowing the solution to stand until the evolution of oxygen has ceased; but as there appears to be no satisfactory indication as to the proper amount of sodium peroxide to be added, resulting in solutions which are not uniformly satisfactory, we have found the following method of oxidation to be more satisfactory.

The colloid solution from which the ammonia has been removed by treatment with Permutit as described above is treated with about one-tenth its volume of Nessler solution, the mixture allowed to stand until clear and the clear solution decanted when it is ready for use.

This colloid solution may be added in amounts to suit the particular case in hand, but the addition of 3 cc. of this solution to 15 cc. of Nessler solution we have found suitable for nearly all cases met in practice. Apparently any of the various modifications of Nessler solution may be used, but we have found it desirable to follow Folin's directions with the exception of making more concentrated, so that after the addition of the colloid solution the final concentration of alkali and mercury will be that given by Folin and Wu.[3]

Standard ammonia solutions for the preparation of Nesslerized standards may be made by suitable dilution of a macro digestion of a material whose nitrogen content has been accurately determined by the usual distillation and titration procedure or from an accurately weighed portion of pure, dry ammonium sulfate. Care must be taken, however, that the standard and unknown solutions when Nesslerized contain as nearly as possible the same concentration of salts. This would seem to be particularly true when iron is present in appreciable amount, as the colloid will hold considerable ferric hydroxide in the colloidal state and this will undoubtably affect the readings, although to what extent we have not as yet determined.

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[3] Folin and Wu, J. Biol. Chem., 38, 81 (1919).

Further work on the method is in progress but owing to the very limited time available for this work it was thought advisable to publish the progress at this time.

Summary

1. A protective colloid prepared from gum arabic has been utilized in the Nesslerization of ammonia in the presence of alkali sulfates.

2. By this method a higher concentration of ammonia nitrogen can be Nesslerized in an ordinary Kjeldahl digestion solution than by previous methods even in the absence of any extraneous salts.

3. The limit of accuracy for the colorimetric determination of nitrogen by this method appears to be the accuracy of the colorimeter readings.

CHAMPAIGN, ILLINOIS

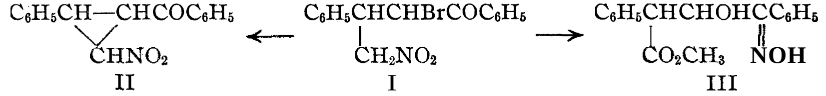
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OR HARVARD UNIVERSITY]

ISOXAZOLINE OXIDES. VIII

BY E. P. KOHLER

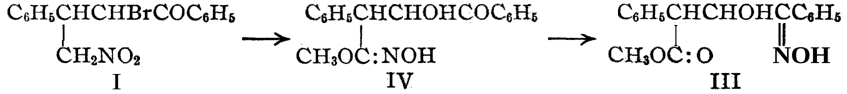
RECEIVED OCTOBER 5, 1927 PUBLISHED JANUARY 5, 1928

It has been shown that cold methyl alcoholic potassium acetate transforms certain α-bromo-γ-nitro ketones into cyclopropane derivatives and hydroxy oximido esters.[1] The oximido esters were unexpected



products. Their discovery led to an investigation of the mechanism by which substances so remotely related are formed from the nitro ketones. The mechanism has not been established completely, but a significant intermediate has been isolated, and the facts which have been accumulated provide a basis for a reasonable explanation.

The method of investigation was based on the fact that no compounds corresponding to the hydroxy oximido esters are formed from bromonitro ketones in which the nitro group is attached to a secondary carbon atom. This observation led to the inference that the oximido esters are formed by rearrangement of some hydroxamic acid derivative because the formation of such derivatives is peculiar to primary nitro compounds. A plausible series of steps would be



For the purpose of testing this hypothesis, methyl alcoholic potassium acetate-was unsuitable because the solution steadily increases in acidity

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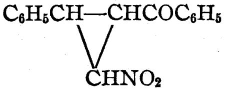
[1] (a) Kohler and Shohan, THIS JOURNAL, 48, 2425 (1926); (b) Kohler and Goodwin, *ibid.*, 49, 219 (1927).

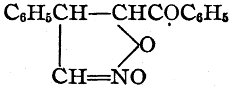
as the reaction progresses. In place of it was used a buffered solution prepared by suspending a large excess of sodium carbonate and sodium bicarbonate in dry methyl alcohol. Towards this solution the two stereomeric bromine compounds represented by I behaved quite differently: the lower-melting isomer gave, mainly, three of the four possible cyclopropane derivatives, while the higher-melting compound yielded, along with cyclopropane derivatives, a substance isomeric with the hydroxy oximido ester. This proved to be the hydroxamic ether represented by IV.

When the hydroxamic ether is shaken or warmed with a methyl alcoholic solution of potassium acetate and acetic acid it passes rapidly and almost quantitatively into the hydroxy oximido ester. It, therefore, doubtless is a real intermediate in the process by which the bromo nitro ketone is converted into the oximido ester. Two problems still remain: to account for the formation of the hydroxamic ether, and to explain the transposition of the oximido group.

With respect to the first problem it is well known that while primary nitro compounds are readily transformed into hydroxamic acids, this occurs only in the presence of acids; bases either form salts of aci-nitro forms or, if too dilute, have no action on the nitro group. Direct experiment showed, moreover, that beyond developing a feeble yellow color, neither potassium acetate nor methyl alcoholic sodium carbonate has any action on the unbrominated nitro ketone. The bromine in the α position, therefore, plays an important part in the process.

In order to provide a proper role for the α bromine atom, and also to account for the fact that the hydroxamic ether is much more readily formed from one of the stereo-isomeric bromine compounds than from the other, one inevitably turns to cyclic intermediates. Two types of cyclic compounds have been obtained by eliminating hydrogen bromide from α-bromo-γ-nitro ketones: nitro cyclopropane derivatives[2] and isoxazoline oxides.[3] In the case under consideration these cyclic products would be represented by II and V.


II


V

Three of the four possible cyclopropane derivatives are in hand. As they are quite insensitive to methyl alcoholic sodium carbonate they cannot be involved in the formation of the hydroxamic ether. All efforts to prepare the oxide V were fruitless, but from the behavior of known oxides and that of analogously constituted furoxanes it is possible to

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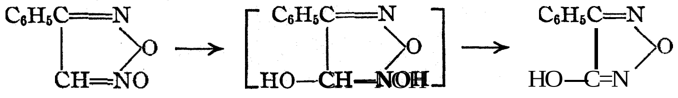
[2] Kohler and Engelbrecht, THIS JOURNAL, 41, 1379 (1919).

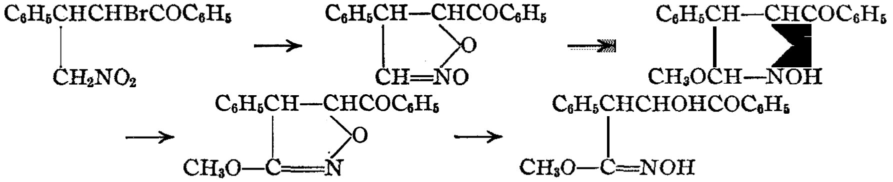
[3] Kohler and Barrett, *ibid.*, **48**, 1770 (1926).

foresee that this oxide would be exceedingly sensitive and that it would be rearranged into more stable substances both by acids and by bases. Its nearest relative, phenylfuroxane VI, in the presence of bases rapidly changes to the hydroxy furazane V11[4]



VI VII

In accordance with this behavior methyl alcoholic sodium carbonate would first transform the isoxazoline oxide into a methoxy isoxazolidine, but since isoxazoline rings are readily opened by bases, the final product would be the hydroxamic ether. The most probable mechanism is, therefore



Inasmuch as acids hydrolyze hydroxamic ethers to esters, and hydroxy ketones readily form oximes in acid solution, the transition from the hydroxamic ether to the oximido ester could be adequately explained by successive hydrolysis and oxime formation. But no free hydroxylamine can be detected at any stage of the process and none can be caught by allowing the reaction to take place in the presence of a large quantity of an aldehyde. It seems at least as probable therefore that the transposition of the oximido group occurs by way of cyclic intermediates. There is at present no experimental evidence on this point.

As a result of this and earlier investigations it now appears certain that whenever hydrogen bromide is eliminated from a-bromo-y-nitro ketones the two possible primary products are nitro cyclopropane derivatives and isoxazoline oxides. Since these nitro cyclopropane derivatives are not attacked either by dilute bases or acids, they can almost invariably be isolated. All isoxazoline oxides are sensitive both to bases and acids; they can consequently be isolated only in favorable cases; usually secondary products appear in place of the isoxazoline oxides. The nature of these secondary products depends on that of the nitro ketone and on the medium in which hydrogen bromide is eliminated. In a basic medium bromo ketones which contain a primary nitro group give either a hydroxamic acid or its ether

$$\underset{\text{HOC:NOH}}{C_6H_5CHCHOHCOC_6H_5} \qquad \underset{CH_3OC\text{:NOH}}{C_6H_5CHCHOHCOC_6H_5}$$

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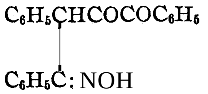
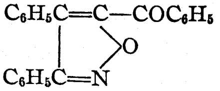
[4] Wieland and Semper, *Ann.*, **358**, 47 (1907).

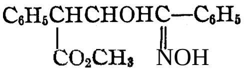
Secondary nitro compounds, under the same conditions, yield either monoximes of triketones or isoxazole derivatives



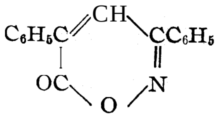
$C_6H_5\underset{C_6H_5C:NOH}{\underset{|}{C}H}COCOC_6H_5$



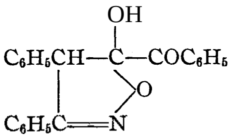
In an acid medium the products from the primary nitro compounds are oximido esters or oxazine derivatives

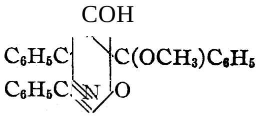


$C_6H_5\underset{CO_2CH_3}{\underset{|}{C}H}CHOH\underset{NOH}{\underset{\|}{C}}-C_6H_5$



The corresponding products from secondary nitro compounds are hydroxy isoxazolines or oxyazines of a different type.

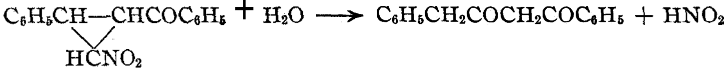




Experimental Part

The reagent used in this investigation—a suspension of anhydrous sodium carbonate in dry methyl alcohol—was first tried separately with each of the stereo-isomeric bromonitro ketones. Both reacted rapidly when the mixture was shaken sufficiently vigorously and both gave a number of products, all of which contained nitrogen.

The methyl alcoholic solution obtained from the lower-melting isomer, when concentrated, readily deposited a large quantity of a solid which was identified as the known cyclopropane derivative melting at 95°. The filtrate left an oil which slowly solidified and from which two additional products melting at 88 and 140° were ultimately isolated. These with cold concentrated sodium alcoholate gave the characteristic reaction of nitro cyclopropane ketones[6]



The solution obtained from the higher-melting isomer likewise first deposited the known cyclopropane derivative but the filtrates from this slowly deposited a much higher-melting solid which was exceedingly difficult to handle until it was discovered that from solutions containing acetone it crystallizes fairly well in tables containing acetone of crystallization.

Analyses and a molecular weight determination showed that this new product is isomeric with the oximido ester. A methoxyl determination proved the presence of one such group and a quantitative examination

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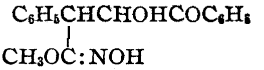
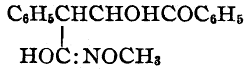
[6] Kohler and Engelbrecht, THIS JOURNAL, 41, 1379 (1919).

of its behavior towards methyl magnesium iodide showed that it consumed three moles of reagent and liberated two moles of methane gas. These analytical results show that the substance contains a methoxyl group, two active hydrogen atoms presumably present as hydroxyl and one group capable of combining with methyl magnesium iodide—probably carbonyl. Unlike the oximido ester, it does not form a copper derivative when its ethereal solution is shaken with copper acetate; it, therefore, does not contain the system —C(OH)C(NOH)—. In combination with the known origin of the substance, these facts leave only two possible formulas

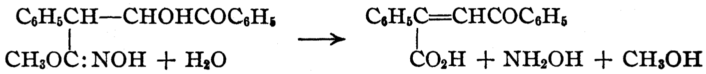


$$\begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ \qquad\quad |\\ CH_3OC{:}NOH\end{array}$$



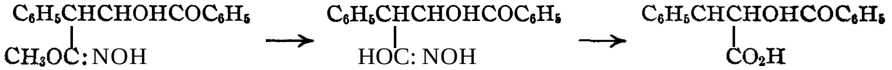
$$\begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ \qquad\quad |\\ HOC{:}NOCH_3\end{array}$$

The first formula is confirmed, the second excluded, by the following transformations. Acetic acid and dilute solutions of mineral acids in methyl alcohol convert the substance into the oximido ester **III,** while concentrated hydrochloric acid in methyl alcohol both hydrolyzes and eliminates water, leaving *trans*-α-phenyl-β-benzoyl acrylic acid.



$$\begin{array}{l}C_6H_5CH{-}CHOHCOC_6H_5\\ \qquad\quad |\\ CH_3OC{:}NOH + H_2O\end{array} \longrightarrow \begin{array}{l}C_6H_5C{=}CHCOC_6H_5\\ \qquad\quad |\\ CO_2H + NH_2OH + CH_3OH\end{array}$$

The substance, while indifferent to weak and dilute bases, dissolves readily in strong alkaline solutions and is reprecipitated by carbon dioxide and other acids. This typical behavior of oximes excludes the second formula. If the alkaline solutions are allowed to stand for some hours before acidification, the result is an acid which gives the characteristic reactions of hydroxamic acids and which can be further hydrolyzed to an hydroxy acid of known structure



$$\begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ \qquad\quad |\\ CH_3OC{:}NOH\end{array} \longrightarrow \begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ \qquad\quad |\\ HOC{:}NOH\end{array} \longrightarrow \begin{array}{l}C_6H_5CHCHOHCOC_6H_5\\ \qquad\quad |\\ \qquad CO_2H\end{array}$$

After a sample of the hydroxamic ether had become available for inoculation it was possible to get the substance by starting with the mixture of stereomeric bromine compounds and, since the separation of this mixture is an exceedingly laborious operation, most of the substance was prepared in this manner. The procedure was as follows.

Fifty grams each of the mixed bromo compounds and anhydrous sodium carbonate were suspended in 300 cc. of dry methyl alcohol. The mixture was vigorously shaken on a mechanical shaker for four hours, then poured into a liter of water. This precipitated a yellow oil which was suspended in a faintly yellow aqueous solution. Four lots were poured together and extracted with ether. The water solution contained only a minute amount of organic material. The ethereal layer was thoroughly washed with water to remove methyl alcohol, then dried over calcium chloride and freed from ether. This left 140–150 g. of bromine-free yellow oil.

The oil was dissolved in 200 cc. of acetone, the solution diluted with 275–300 cc.

of petroleum ether, then inoculated with a sample of the hydroxamic ether which had been recently recrystallized from acetone-petroleum ether and set aside. In the course of twenty-four hours it gradually deposited 24–26 g. of fairly pure ether in well-formed tables, and 3-4 g. more of less pure substance separated in the course of a week. After purification by recrystallization from the same mixture of solvents the total yield was 21 g.

The filtrate from the hydroxamic ether was freed from acetone and petroleum ether, the oil dissolved in 300 cc. of warm methyl alcohol, the solution inoculated with the cyclopropane derivative melting at 95°, then gradually cooled, finally to —20". It deposited 75–100 g. of almost pure product. The filtrate from this, when allowed to evaporate very slowly in covered beakers, finally turned into a pasty mush. By draining off the liquid at a low temperature with a pump and patiently recrystallizing the solid from ether-petroleum ether this was finally separated. It yielded 3 substances, the known cyclopropane derivative melting at 95°, and two new cyclopropane derivatives melting, respectively, at 88° and 140–142°.

The Cyclopropane Derivatives

The new cyclopropane derivatives crystallize in fine needles. They resemble each other so closely that it is impossible to distinguish them except by melting point and solubility.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.9, H, 5.0 Found: I (88°): C, 71.9; H, 5.2; II (140°): C, 72.0; H, 4.9.

Each of these substances was dissolved in concentrated sodium methylate as directed in an earlier paper.[6] The lower-melting compound gave 3.5, the higher-melting 3.1 g., of the copper derivative of benzoyl phenacetyl methane—proving that these substances are stereo-isomers of the known benzoyl phenyl nitro cyclopropane.

The Hydroxamic Ether. IV

The ether crystallizes from acetone in transparent tables containing one molecule of acetone which is slowly given off at the ordinary temperature.

Anal. Calcd. for $C_{17}H_{17}O_4NC_3H_6O$: C, 67.6; H, 6.9. Found: C, 67.4; H, 7.1.

When the substance is pure, it can be recrystallized from ether and petroleum ether from which it separates in small, thick plates which are free from solvent.

Anal. Calcd. for $C_{17}H_{17}O_4N$: C, 68.2; H, 5.8; OCH_3, 10.2. Found: C, 68.4; H, 6.0; OCH_3, 10.2.

The ether is extremely soluble in alcohol and in acetone, moderately soluble in ether, insoluble in petroleum ether. It melts with decomposition at about 190°.

Behavior **toward** Bases.—The hydroxamic ether dissolves readily in excess of cold 20% aqueous sodium hydroxide. If the resulting pale yellow solution is immediately acidified all of the ester is recovered; if it is shaken with acetic anhydride it deposits a mono-acetate of the ester; and if it is kept for some hours and then acidified the product is the corresponding hydroxamic acid.

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[6] Kohler and Engelbrecht, THIS JOURNAL, 41, **1383** (1919).

The Acetate.—The acetate is most readily made by dissolving the ether in acetic anhydride, warming the solution for a few minutes on a steam-bath and then pouring it into ice water. It crystallizes from ether and from methyl alcohol in stout needles, from ether-petroleum ether in prisms. It melts with effervescence at about 185°.

Anal. Calcd. for $C_{19}H_{19}O_5N$: C, 66.9; H, 5.6; OCH_3, 9.1. Found: C, 66.8; H, 5.7; OCH_3, 8.4.

The Hydroxamic **Acid.—A** solution of 10 g. of the hydroxamic ether in excess of 10% aqueous sodium hydroxide was kept for five hours at the ordinary temperature, then extracted with ether. This removed 0.4 g. of unchanged hydroxamic ether. The alkaline solution was cooled in ice water, covered with 25 cc. of ether and acidified with iced dilute sulfuric acid. The ethereal layer promptly began to deposit colorless needles melting with decomposition at about 160". The aqueous layer, even though it had been extracted with ether five times, deposited another gram of the same acid in the course of a week; total yield of crude product, 7.2 g.

The acid is extremely difficult to purify because in solution it gradually changes to a more soluble acid. From a mixture of ether and petroleum ether it occasionally separated in well-formed tables.

Anal. **Calcd.** for $C_{16}H_{15}O_4N$: C, 67.3; H, 5.3. Found: C, 67.1; H, 5.1:

The acid is readily soluble in alcohol, moderately soluble in ether, sparingly soluble in water. It forms a khaki-colored copper compound both when its ethereal and when its aqueous solution is shaken with copper acetate. Both ethereal and aqueous solutions also give blood-red solutions when they are added to methyl alcoholic ferric chloride. In polar solvents the hydroxamic acid apparently undergoes a spontaneous rearrangement into the isomeric oximido ester. Thus in an attempt at recrystallization a solution of 2 g. of the acid in methyl alcohol was diluted with water until it was definitely turbid. In the course of a few days the turbidity disappeared and the solution then gave a vivid green instead of a khaki-colored copper compound. Upon inoculation it deposited 1.4 g. of the isomeric oximido acid melting at 168°.[1b]

Behavior of the **Hydroxamic** Ether toward Acids.—The sole action of acids on the hydroxamic ether appears to be its rearrangement to the isomeric oximido ester, for while other products can be obtained by vigorous treatment with mineral acids, all of these are also formed by similar treatment of the oximido ester. The rearrangement can be brought about almost quantitatively with methyl alcoholic potassium acetate and acetic acid. Thus a solution of 2 g. of the ether, 2 g. of the acetate and 5 cc. of acetic acid in 20 cc. of dry methyl alcohol was boiled for half an hour, then cooled and poured into ether and water. The ethereal layer was shaken with sodium carbonate, washed with water, dried and concentrated. It gave 1.72 g. of pure oximido ester and a small quantity of a contaminated product.

Trans-α-phenyl-β-benzoyl Acrylic Acid

The unsaturated ketonic acid is the final product in the degradation of the hydroxamic ether by acids. It is formed when the ether itself, the hydroxamic acid, the oximido ester, the oximido acid or the ketonic acid is heated with methyl alcoholic hydrochloric acid. This was established by heating each of these substances for several hours with a mixture of equal volumes of methyl alcohol and concentrated hydrochloric acid. The best yield (80%) was obtained from the oximido ester. The acid is readily soluble in acetone and alcohol, sparingly in ether. It was purified by crystallization from a mixture of acetone and petroleum ether, from which it separates in small, lustrous tables melting without decomposition at 202°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Pound: C, 76.5; H, 4.8.

Structure.—An aqueous solution of permanganate was dropped into *a* cold and rapidly stirred solution of 2 g. of the acid in sodium bicarbonate until the permanganate color persisted for fifteen minutes. The oxide of manganese was dissolved by adding sulfur dioxide, the solution strongly acidified and extracted with ether. The dried ethereal solution, on evaporation, left a residue weighing 2.18 g. With phenylhydrazine this gave 3.05 g. of a phenylhydrazone melting at 161–162°, and identified as the hydrazone of phenyl glyoxylic acid by comparison with *a* sample on hand. Oxidation with permanganate, therefore, ends in two molecules of phenyl glyoxylic acid.

Synthesis.—Although the result of oxidation left no doubt as to the structure of the unsaturated acid it seemed best to synthesize it because it does not, like the isomer described in an earlier paper,[7] give an oxazine when treated with hydroxylamine. The synthesis by way of α-phenyl-β-benzoyl propionic acid presents no difficulties. When this ketonic acid is brominated it gives two isomeric β-bromo derivatives melting, respectively, at 195 and 208°, both with decomposition. The lower-melting compound crystallizes from ether in large prisms containing ether of crystallization which is lost at the ordinary temperatures.

Anal. Calcd. for $C_{16}H_{13}O_3Br$: C, 57.7; H, 3.9. Found: C, 57.5; H, 4.0.

This bromo compound readily dissolves in an equivalent quantity of normal aqueous sodium carbonate, but it soon becomes cloudy and in the course of a week it deposits a considerable quantity of crystalline material composed of the acid and an indifferent compound which will be described elsewhere. The mixture was easily separated by extraction with sodium carbonate. The acid obtained in this manner was the same as that formed by the hydrolysis of the hydroxamic acid.

Summary

An investigation of the process by which methyl alcoholic potassium acetate transforms certain a-bromo-y-nitro ketones into β-hydroxy-γ-oximido esters leads to the conclusion that the primary product of the reaction is an isoxazoline oxide. Potassium acetate first transforms this into an hydroxamic ether, which was isolated, and the acetic acid formed in the reaction rearranges the hydroxamic ether to the oximido ester.

CAMBRIDGE 38, MASSACHUSETTS

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[7] Ref. 1 b, p. 226.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

5-BROMO-2,4-DIMETHOXYBENZOYLACRYLIC ACID AND ITS ESTERS

BY GRACE POTTER RICE

RECEIVED OCTOBER 19, 1927 PUBLISHED JANUARY 5, 1928

The work described in this paper was begun with the intention of studying a dimethoxy substituted benzoylacrylic acid and its esters but the method used in the attempt to prepare them from dimethoxybenzoylpropionic acid gave unsaturated substances with a bromine atom in the ring; the methyl ester has been shown to be methyl-5-bromo-2,4-dimethoxybenzoylacrylate.[1] The fact that the acid as well as its methyl and ethyl esters have melting points much higher than those of the various unsaturated ketonic acids and esters previously investigated in this Laboratory[2] suggested that they might be desirable substances for evidence of any possible relationship between the melting point of a solid which is sensitive to light and its tendency to isomerize or polymerize. No evidence on this point is obtained from the study of 5-bromo-2,4-dimethoxybenzoylacrylic acid (208") and its methyl ester (129°), for they do not polymerize or isomerize in the sunlight. The ethyl ester, however, is extremely sensitive to light and since a low-melting substance on exposure to light usually isomerizes like a substance in solution because it melts and behaves in the molten condition as though it were in solution,[3] this ethyl ester, with its melting point of 115.5°, would not be expected to isomerize but to polymerize as is usually the case with solids in the dry condition. It has been found that the ethyl ester is rapidly changed to a polymer which is probably a cyclobutane derivative; it is the only unsaturated ketonic ethyl ester of the five investigated to form a polymer and the only one with a melting point above 55°.

The tendency of a bromine atom in the ring to favor the formation of crystalline substances has made possible the investigation of reactions with this ketonic acid which could not be studied with benzoylacrylic acid and its simpler substitution products. Such a reaction is that which the methyl ester of 5-bromo-2,4-dimethoxybenzoylacrylic acid undergoes in methyl alcohol solution containing a trace of potassium hydroxide. Two structural isomers are possible which are a result of 1:4 addition to the two conjugated systems of double linkages in the ester, $(CH_3O)_2C_6H_2Br\underset{1}{O}\underset{2}{C}\overset{4}{\underset{3}{C}}H=$

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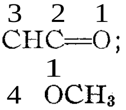
[1] Rice, THIS JOURNAL, 48, 3125 (1926).

[2] Rice, *ibid.*, 45, 222 (1923); 46, 214, 2319 (1924); 48,269 (1926).

[3] (a) Stobbe, *Ber.*, 52, 666 (1919); (b) Stobbe and Steinberger, *Ber.*, 55, 2225 (1922); (c) Stobbe and Lehfeldt, *Ber.*, 58, 2415 (1925).



$\overset{3}{\mathrm{C}}\mathrm{H}\underset{\substack{1\\ \mathrm{OCH_3}}}{\overset{2}{\mathrm{C}}}=\overset{1}{\mathrm{O}}$ (4); if the $(COOCH_3)$ determines the addition, the product would be a β-methoxy ester, $(CH_3O)_2C_6H_2BrCOCHOCH_3CH_2CO_2CH_3$, but if the (CO) determines the addition, the product would be an a-methoxy ester, $(CH_3O)_2C_6H_2BrCOCH_2CHOCH_3CO_2CH_3$. The proof that the latter is the case rests on the fact that the β-methoxy ester was prepared in a way which left no doubt as to its structure and it was found to be not identical but isomeric with the methoxy ester formed in the addition reaction. The results of further study of the bromodimethoxy acid and its esters will be reported later.

Experimental Part

2,4-Dimethoxybenzoylpropionic acid[4] was prepared from resorcinol dimethyl ether and succinic anhydride by the Friedel and Crafts reaction. After the dark red solid addition product had been decomposed with water, steam was forced through the mixture until the carbon disulfide and resorcinol dimethyl ether were removed. The colorless product which crystallized from the hot aqueous solution was a mixture of acids and a mixture was always obtained though the conditions of carrying out the reaction were varied in an attempt to find the factors favoring the formation of pure dimethoxy acid. The crude product—75 to 85%—was separated partially after several recrystallizations from 50% acetic acid to give a yield of 65–75% of pure dimethoxy acid. The residue was still a mixture which was shown to contain 2-hydroxy-4methoxybenzoylpropionic acid by isolation of the methyl ester of this acid melting at 87°[4] on esterification of the residue; the acid itself was not separated.

Anal. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.88. Found: C, 60.28; H, 5.95.

β-Bromo-5-bromo-2,4-dimethoxybenzoylpropionic Acid, $(CH_3O)_2C_6H_2BrCOCHBrCH_2CO_2H$.—The bromo acid is formed when the dimethoxy acid is suspended in chloroform and treated with bromine; on evaporation of the chloroform it was left as a solid which was purified by recrystallizing it first from glacial acetic acid and then from methyl alcohol. It separates from both solvents in colorless needles melting at 165° with decomposition. When the crude acid was recrystallized from methyl alcohol it was changed completely into its methyl ester, esterification apparently being brought about by the hydrogen bromide held by the solid.

Anal. Calcd. for $C_{12}H_{12}O_5Br_2$: C, 36.36; H, 3.03. Found: C, 36.54; H, 3.59.

5-Bromo-2,4-dimethoxybenzoylacrylic Acid, $(CH_3O)_2C_6H_2BrCOCH{=}CHCO_2H$.—The unsaturated acid was prepared by heating a concentrated glacial acetic acid solution of the bromo acid with potassium acetate in a boiling water-bath for two hour-,. It crystallized as the solution cooled, was filtered off, washed with water and dried; it is sparingly soluble in boiling water, soluble in boiling methyl alcohol, acetone, benzene, chloroform and glacial acetic acid and almost insoluble in ether. It was purified with

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[4] Perkin and Robinson, J. *Chem. Soc.*, 93, 506 (1908).

both benzene and glacial acetic acid as solvents—yield 95–99% calculated from the saturated acid. The bright yellow needles melt at 208°.

Anal. Calcd. for $C_{12}H_{11}O_5Br$: C, 45.71; H, 3.49. Found: C, 46.10; H, 3.52.

The unsaturated acid can be prepared most readily by brominating a glacial acetic acid solution of the saturated acid and heating this solution of the bromo acid in boiling water for two hours with potassium acetate. The acid which separates on adding a few drops of concd. hydrochloric acid and cooling the solution in an ice-bath melts at 205–208° and the yield is practically quantitative.

5-Bromo-2,4-dimethoxybenzoylpropionic Acid, $(CH_3O)_2C_6H_2BrCOCH_2CH_2COOH$.—This acid was obtained in 75% yield by treating a suspension of unsaturated acid cooled in ice with an aqueous solution of sodium hydrosulfite. The solid which separated on diluting and acidifying the solution was pure and melted at 187° after two recrystallizations from methyl alcohol.

Anal. Calcd. for $C_{12}H_{13}O_5Br$: C, 45.42; H, 4.10. Found: C, 45.62; H, 4.20.

The unsaturated acid is so sparingly soluble in cold ether and benzene that it is not practical to study the action of sunlight on the acid in these solvents; a solution of it in glacial acetic acid was exposed for three months but there was no change in the substance except for a slight amount of decomposition. After exposure for the same length of time, the powdered unsaturated acid was still yellow; a change in melting point of the solid, however, may indicate a very slow formation of a polymer but such a substance was not isolated.

The methyl ester of dimethoxybenzoylpropionic acid was obtained in quantitative yield by heating a methyl alcohol solution of the pure acid for two hours with concd. sulfuric acid; the solution was poured onto cracked ice, powdered sodium carbonate was added as long as solid ester continued to separate and the ester was filtered off, washed with ice water and dried. It can be used without recrystallization for preparation of the unsaturated ester. It separates from methyl alcohol with solvent of crystallization in heavy, transparent needles melting at 49°; they become opaque after several hours and melt at 58–59°, the melting point given by Perkin and Robinson.[4]

When this ester was treated in chloroform solution with one molecular equivalent of bromine under most carefully regulated conditions for bromination, the residue, after removal of the solvent, was an oil which failed to crystallize and which gave an untractable mixture on treatment with potassium acetate. The only unsaturated substance separated from the mixture held a bromine atom, so after the reaction had been repeated several times with the same results, it was deemed useless to try to prevent a bromine atom from entering the ring. Therefore, in subsequent work with this ester, as well as with the ethyl ester and the acid, two molecular equivalents of bromine were used for bromination.

Methyl-β-bromo-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCHBrCH_2CO_2CH_3$.—A chloroform solution of the ester of the dimethoxy acid, cooled in an ice-bath, was treated with two molecular equivalents of bromine and the solvent removed by drawing dry air through the solution. The residue was a cake of crystalline solid which melted at 103° after two recrystallizations from methyl alcohol.

Anal. Calcd. for $C_{13}H_{14}O_5Br_2$: C, 38.05; H, 3.41. Found: C, 38.10; H, 3.54.

Methyl-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH{=}CHCO_2CH_3$.—The methyl alcohol solution of the bromo ester, 20 g. in 200 cc. of methyl alcohol, was boiled for two hours with 10 g. of potassium acetate. The yellow unsaturated ester which separated in long needles as the solution cooled was filtered off, washed with ice water and dried; yield, 97%. After removal of the chloroform, the bromo ester can be used without purification for the preparation of the unsaturated ester; yield, 95–98%. The ester is soluble in boiling benzene, methyl alcohol, acetone, chloroform and glacial acetic acid and all of these solvents can be used for recrystallizing it. On melting it behaves like a substance holding solvent of crystallization; the solid after recrystallization from methyl alcohol softens at 129° and melts at 138°, solidifies on cooling and melts sharply at 129°. The point where the ester softens varies somewhat with specimens recrystallized from different solvents but the melting point of the re-solidified substance is always 129°.

Anal. Calcd. for $C_{13}H_{13}O_5Br$: C, 47.41; H, 3.95. Found: C, 47.11; H, 4.03.

The unsaturated ester is hydrolyzed extremely slowly by boiling with 10% sodium carbonate solution but more readily by boiling with dilute hydrochloric acid to give the unsaturated acid.

Methyl-5-**bromo-2,4-**dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCH_2CH_2CO_2CH_3$.—This substance was formed when an ice-cold methyl alcohol solution of the ester was treated with sodium hydrosulfite; the solid which was precipitated when the solution was diluted with ice water separated from methyl alcohol in fine, colorless needles melting at 117°.

Anal. Calcd. for $C_{13}H_{15}O_5Br$: C, 47.13; H, 4.53. Found: C, 47.10; H, 4.45.

Hydrolysis of this ester gave the corresponding acid melting at 187'.

The yellow, unsaturated ester was recovered unchanged from its benzene solution which had been exposed to the sunlight; when it was exposed as a powdered solid 70% was recovered unchanged and the rest was a brown, amorphous mass from which no crystalline substance could be separated.

Ethyl-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_3COCH_2CH_2CO_2C_2H_5$.—An absolute alcohol solution of dimethoxybenzoylpropionic acid containing concd. sulfuric acid was refluxed for two hours; the solid ester which separated when the solution was poured onto ice was filtered off and washed with ice water. On recrystallization from alcohol large, transparent crystals were obtained which melted at 44°, slowly became opaque, and melted at 68.5"; yield, 94%.

Anal. Calcd. for $C_{14}H_{18}O_5$: C, 63.15; H, 6.76. Found: C, 63.14; H, 6.89.

Ethyl-β-bromo-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCHBrCH_2CO_2C_2H_5$.—A chloroform solution of the ester was treated with two molecular equivalents of bromine, the solvent removed and the solid recrystallized once from alcohol. It separated in thick needles melting at 114.5'; yield, 97%.

Anal. Calcd. for $C_{14}H_{16}O_5Br_2$: C, 39.62; H, 3.77. Found: C, 39.77; H, 4.07.

Ethyl-5-**bromo-2,4-dimethoxybenzoylacrylate,** $(CH_3O)_2C_6H_2BrCOCH{=}CHCO_2C_2H_5$.—The unsaturated ester is formed when the bromo ester is refluxed for two hours with potassium acetate. The ester which crystallized as the solution cooled was filtered off and washed with ice water; it is soluble in boiling organic solvents and crystallizes from benzene and alcohol in firm, yellow plates melting at 115.5'; yield of pure product 96%.

Anal. Calcd. for $C_{14}H_{15}O_5Br$: C, 48.97; H, 4.37. Found: C, 48.79; H, 4.25.

In subsequent preparations, the bromo ester was used without recrystallization for making the unsaturated ester.

Action of Sunlight on **Ethyl-5-bromo-2,4-dimethoxybenzoylacrylate**

The yellow ethyl ester undergoes a remarkably rapid change when powdered and exposed to the sunlight. The colorless solid formed was boiled with several portions of alcohol which left undissolved a substance melting at 265° and practically insoluble in all the common organic solvents; from **6.1** g. of ester, **5.3** g. was obtained (87%). **It** is soluble in boiling nitrobenzene and separates completely from a saturated solution in transparent plates melting at **266°**; its molecular weight was determined in nitrobenzene with the use of a Woods metal bath to insure regular boiling of the solvent.

Anal. Calcd. for $(C_{14}H_{15}O_5Br)_2$: C, 48.97; H, 4.37; mol. wt., 686. Found: C, 48.64; H, **4.27;** mol. wt., 713.

The polymer is stable in the dark but it gradually turns yellow when left in diffused daylight.

From the alcohol a small quantity of substance (129–130°) was separated which did not react with bromine and was stable to light in benzene solution in the presence of iodine; a molecular weight determination by the Rast method indicated that the substance has twice the molecular weight of the unsaturated ester. Its behavior, however, was irregular, for the camphor solution was yellow after the solid mixture had been melted several times and each successive melting point of this yellow solid was lower, showing that depolymerization was taking place. Evidently this polymer is not stable at the melting point of camphor, 178°.

Anal. Calcd. for $(C_{14}H_{15}O_5Br)_2$: C, 48.97; H, 4.37. Found: C, 49.11; H, 4.59.

Reaction of Unsaturated Methyl Ester in Methyl Alcohol Solution Containing a Trace of Potassium Hydroxide

Methyl-α-methoxy-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCH_2CHOCH_3CO_2CH_3$, and **α-Methoxy-5-bromo-2,4-dimethoxybenzoylpropionic** Acid, $(CH_3O)_2C_6H_2BrCOCH_2CHOCH_3CO_2H$.—A mixture of these substances is obtained when a methyl alcohol solution of methyl-5-bromo-2,4-dimethoxybenzoylacryle, cooled in a freezing mixture, is stirred vigorously for three minutes with a few drops of potassium hydroxide solution (2:3). If sufficient solvent was used to keep the unsaturated ester in solution at the low temperature of the reaction, the methoxy acid was the chief product formed; if a suspension of the unsaturated ester was used, the methoxy ester separated at once and could be filtered off, but it was mixed with unsaturated ester which had escaped reaction, and if stirring was continued, in this case, until the yellow ester had reacted completely considerable hydrolysis of the methoxy ester took place and both the methoxy acid and ester were contaminated with sticky yellow decomposition products. The reaction can be carried out with the speed necessary for its success if the unsaturated ester (3 g.) is dissolved in hot methyl alcohol (150 cc.) and enough chloroform added to prevent the ester from crystallizing when the solution is cooled. After stirring for three minutes with a few drops of potassium hydroxide solution, the mixture was acidified with concd. hydrochloric acid, the lower chloroform layer drawn off and the upper layer extracted once with chloroform. Evaporation of the solvent left 3.3 g. of solid which gave, after four recrystallizations from methyl alcohol, 2.9 g. of methoxy ester (117°) and **0.3** g. of methoxy acid (189°), a quantitative yield. The ester is soluble in cold chloroform, hot ether, benzene and methyl alcohol; it crystallizes from benzene and methyl alcohol in fine, colorless needles. The acid is sparingly soluble in ether, benzene and hot chloroform and extremely soluble in methyl alcohol; it is purified most readily by recrystallization from a mixture of methyl alcohol and chloroform.

Anal. (117°). Calcd. for $C_{14}H_{17}O_6Br$: C, 46.53; H, 4.70; mol. wt., 361. Found: C, 46.57; H, 4.83; mol. wt., 357.

Anal. (189°). Calcd. for $C_{13}H_{15}O_6Br$: C, 44.95; H, 4.32. Found: C, 44.92; H, 4.30.

The methoxy acid was also obtained when β-bromo-5-bromo-2,4-dimethoxybenzoylpropionic acid was treated cautiously in ice-cold methyl alcohol solution with sodium methylate. The methoxy acid can be changed into its methyl ester by the usual esterification methods and the ester can be hydrolyzed by very cautious treatment with alkali to give the methoxy acid. When the methoxy ester was heated for two hours on a water bath with dil. hydrochloric acid (1:2) about equal parts of unsaturated acid and unsaturated methyl ester were obtained.

Synthesis of α- and β-Hydroxy Acids

α-Hydroxy-5-bromo-2,4-dimethoxybenzoylpropionic Acid, $(CH_3O)_2C_6H_2BrCOCH_2CHOHCO_2H$.—This acid was formed when the unsaturated acid and its methyl ester were boiled with dilute hydrochloric acid for many hours, but even after repeated attempts an amount of it sufficient for preparation of the ester of its ether was not accumulated. It is readily soluble in water, alcohol and hot chloroform; from chloroform it separates in fine needles melting at 172°.

Anal. Calcd. for $C_{12}H_{13}O_6Br$: C, 43.24; H, 3.90. Found: C, 43.84; H, 3.86.

β-Hydroxy-5-bromo-2,4-dimethoxybenzoylpropionic Acid, $(CH_3O)_2C_6H_2BrCOCHOHCH_2COOH$.—Since the α-hydroxy acid could not be obtained in quantity, the β-hydroxy acid was prepared in order to compare the ester of its ether with the methoxy ester (117°). A mixture of 14 g. of β-bromo-5-bromo-2,4-dimethoxybenzoylpropionic acid and 1000 cc. of 10% sodium carbonate solution was shaken in a machine for three hours; on acidification a solid was precipitated which crystallized from methyl alcohol and from water in colorless needles melting at 179° with decomposition; yield of pure acid 80%.

Anal. Calcd. for $C_{12}H_{13}O_6Br$: C, 43.24; H, 3.90. Found: C, 43.32; H, 3.76.

Methyl-β-methoxy-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCHOCH_3CH_2CO_2CH_3$.—This substance was formed when a methyl alcohol solution of the β-hydroxy acid was heated for eleven hours on a water-bath with methyl iodide and silver oxide; it crystallizes from methyl alcohol in needles melting at 134.5°.

Anal. Calcd. for $C_{14}H_{17}O_6Br$: C, 46.53; H, 4.70. Found: C, 46.71; H, 4.77.

Since this is the methyl ether of the β-hydroxy ester, the methoxy ester melting at 117° must have its methoxy group in the α position.

Reaction of Unsaturated Ethyl Ester in Alcohol Solution Containing a Trace of Potassium Hydroxide

Ethyl-α-ethoxy-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCH_2CHOC_2H_5CO_2C_2H_5$ and **α-Ethoxy-5-bromo-2,4-dimethoxybenzoylpropionic Acid** $(CH_3O)_2C_6H_2BrCOCH_2CHOC_2H_5CO_2H$.—These substances are formed when an absolute alcohol solution of the unsaturated ethyl ester is treated with alkali in the manner described in the reaction with the unsaturated methyl ester. The ethoxy ester is readily soluble in ether, chloroform and hot methyl and ethyl alcohols; it crystallizes from alcohol in needles melting at 97°.

Anal. Calcd. for $C_{16}H_{21}O_6Br$: C, 49.35; H, 5.39. Found: C, 49.52; H, 5.52.

The ethoxy acid (139–140°) is soluble in alcohol, chloroform and boiling benzene, sparingly soluble in ether and petroleum ether; it can be recrystallized from benzene, from alcohol and from a mixture of chloroform and petroleum ether.

Anal. Calcd. for $C_{14}H_{17}O_6Br$: C, 46.53; H, 4.70. Found: C, 46.47; H, 4.65.

The ethoxy acid was obtained in 50% yield by cautious hydrolysis of the ethoxy ester with alcoholic potassium hydroxide and was separated from the unsaturated acid which is also formed by taking advantage of the lack of solubility of the latter in cold chloroform.

When the unsaturated ethyl ester was treated with potassium hydroxide in the presence of methyl alcohol in the way described for the unsaturated methyl ester, a 69% yield of the methyl ester of the methoxy acid was formed; likewise the unsaturated methyl ester in the presence of ethyl alcohol gave an 80% yield of the ethyl ester of the ethoxy acid. In neither reaction was a second substance found; the poorer yields than were obtained when the reaction was carried out with an ester in the presence of the corresponding alcohol are accounted for by the formation, in both cases, of a considerable amount of yellow decomposition product.

Summary

5-Bromo-2,4-dimethoxybenzoylacrylic acid and its methyl ester are not isomerized or polymerized in the sunlight; the ethyl ester is stable to light in benzene solution but it is rapidly polymerized when exposed as a solid. Hydrolysis of the esters with sodium carbonate solution is extremely slow and incomplete; the methyl ester gives the unsaturated acid and *a* trace of a-hydroxy-5-bromo-2,4-dimethoxybenzoylpropionic acid on boiling for many hours with dilute hydrochloric acid. These esters react in methyl and ethyl alcohol solution in the presence of a few drops of potassium hydroxide solution to give α-alkoxyl addition products which are a result of 1:4 addition to one of the two conjugated systems of double linkages present in the esters.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE RELATION OF THE STRUCTURE OF KETONES TO THEIR REACTIVITY AND AFFINITY IN ACETAL FORMATION

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The reaction of ketones with alcohols to form acetals analogous to the reaction of aldehydes with alcohols proceeds to so slight an extent, if at all, that the reaction is of no importance. In order to form the acetal of the ketones it is necessary to react the ketones with an ortho ester according to the equation $R_2C{=}O + HC(OR')_3 \qquad R_2C(OR')_2 + HCO_2R'$. The reaction like that of aldehydes with alcohols is a reversible one and hence may be used for the evaluation of the relation of the structure of a ketone to the strength of the linkage between oxygen and carbon in the acetal.[1,2,3] To this end the extent of the reaction of eight ketones

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[1] Adkins and Adams, THIS JOURNAL, 47, 1377 (1925).

[2] Hartung and Adkins, *ibid.*, 49, 2517 (1927).

[3] Street and Adkins, *ibid.*, 50, 162 (1928).

with orthoformic ester has been determined. The ketones whose. reactions have been investigated include five methyl ketones in which the second radical was methyl, ethyl, *n*-hexyl, phenyl or tertiary butyl, besides diethyl, diphenyl and propylphenyl ketones.

The reaction of the ketone with orthoformic ester did not proceed in a toluene or xylene solution containing hydrogen chloride, but proceeded smoothly in an alcoholic solution containing hydrogen chloride as a catalyst. It is apparently necessary to have a considerable proportion of alcohol in the solution, at least in some cases, for 0.1 mole of phenylpropyl ketone did not react with 0.12 mole of orthoformic ester in the presence of 4 cc. of ethanol but the reaction proceeded readily with 14 cc. of alcohol, the amount of hydrogen chloride being constant.

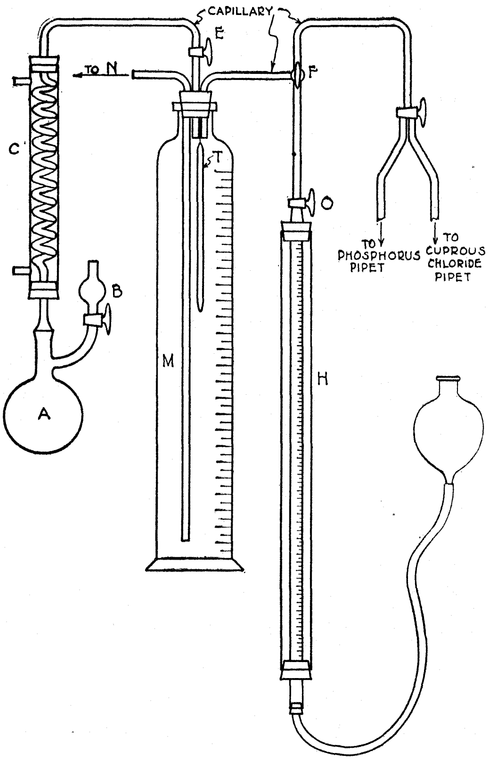

Fig. 1.—Apparatus for analysis for ethyl formate.

A typical procedure for an experiment was as follows. One-tenth of a mole (7.35 cc.) of acetone was run from a standard buret into a Pyrex test-tube (25 X 3.5 cm.). Twenty cubic centimeters or 0.1268 of a mole of orthoformic ester was added, followed by 11.65 cc. of absolute alcohol. A sampling device similar to that described by Child[4] was connected to the test-tube and the test-tube placed in a thermostat at 25°. After allowing the contents of the tube to come to the temperature of the thermostat, 1 cc. of alcohol containing 0.0136 g. of hydrogen chloride was added through the sampling device and thoroughly mixed with the contents of the tube by several times drawing the liquid up into the sampling device and allowing it to run back into the test-tube. After 48 to 60 hours a 5cc. sample was withdrawn and analyzed for ethyl formate. The time interval was chosen after it had been ascertained by experiment that the reaction had gone to completion in that time.

The retrograde reactions were run upon the diethyl acetals of acetone, acetophenone, diethyl ketone and methyl-n-hexyl ketone. Again, acetone diethyl acetal is given as typical. One-tenth of a mole of the diethyl acetal of acetone was put into a Pyrex test-tube, 0.1 mole of ethyl formate was added, together with sufficient alcohol to make the volume of the reaction mixture the same as that in the synthetic reaction. The test-tube was placed in a thermostat and, when the contents had reached 25°, 1 cc. of ab-

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[4] Child and Adkins, THIS JOURNAL, **45**, 3020 (1923).

solute alcohol containing 0.0136 g. of hydrogen chloride was added through the sampling device. After standing 48–60 hours a 5cc. sample was withdrawn and analyzed.

The method for the determination of ethyl formate was developed by making use of Geuther's observation that sodium ethoxide catalyzes the decomposition of the ester into carbon monoxide and alcohol.[5] An apparatus, a diagram of which is shown in Fig. 1, was developed in which ethyl formate was decomposed by sodium ethoxide and the evolved gas collected and analyzed for carbon monoxide. Such an analysis was conducted in the following manner.

One-half of a gram of sodium ethoxide was placed in the 50cc. flask (A) connected to a 20cm. spiral condenser (C) by a rubber stopper sealed in with collodion. The sample was run into the side-arm bulb (B) from which it was allowed to run into the flask through a stopcock. Ice water was placed about the flask in order to absorb the heat generated at the beginning of the reaction; otherwise the temperature in the flask would rise so rapidly that some of the ethyl formate would volatilize and condense on the cooler portions of the flask and condenser before reacting with the sodium ethoxide. Two cc. of dry toluene was poured down the sides of the side arm and bulb to wash down any of the ester which might be adhering to the sides of the glass. The evolved gas passed up through the condenser and replaced the saturated salt solution in the graduated container (M), the replaced liquid passing into a second graduated container (N). The level of the liquid in (N) was maintained slightly lower than that of the liquid in (M), so that no back pressure would be set up. After five minutes the ice-bath was replaced by a paraffin oil-bath which was gradually heated until it attained a temperature of 110–115° and this temperature was maintained for about one hour. All of the gas in the flask, condenser coils and connecting capillary tubing was forced into (M) by passing a saturated salt solution into the system through the side arm (B). The three-way stopcock (E) was closed and the container (N) was adjusted so that the level of the solution in it was the same as that in (M). The volume of gas in (M) was recorded and the temperature of the gas was obtained from the thermometer (T) which was immersed in it. The barometric pressure was recorded. A thorough mixing of the gas in (M) was accomplished by drawing a portion of it into the volumetric buret (H) and then passing it back into (M) eight or ten times until, finally, a 100cc. portion was confined in (H) by closing the three-way stopcock (F). This aliquot was analyzed for carbon monoxide, after removing the oxygen over phosphorus. The carbon monoxide was absorbed in acid cuprous chloride. The time required to decompose the ethyl formate and analyze the resulting gas was from one and three-quarters to two hours.

The presence of ethyl alcohol was found by Geuther to inhibit the decomposition of ethyl formate. This difficulty was overcome by adding a small piece of sodium, in slight excess of the amount necessary to react with all the alcohol formed. The presence of toluene and orthoformic ester did not affect the amount of carbon monoxide evolved. It was found that the amount of sodium ethoxide used to decompose ethyl formate did not influence the amount of carbon monoxide evolved, in most experiments 0.5 g. of sodium ethoxide being used. The analysis of nineteen samples of known and varying ethyl formate content showed that the amount of carbon monoxide formed was 64.6% ± 1.5% of that required by the equation given by Geuther, $HCO_2C_2H_5 \rightleftarrows CO + C_2H_5OH$. The course of this reaction will be considered later; suffice it for the present

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[5] Geuther, *Chem. Cent.*, **39**, 632 (1868).

to say that apparently approximately three molecules of the ester yield two molecules of carbon monoxide. Not a trace of carbon dioxide was detected when over three liters of the evolved gas was passed through a solution of barium hydroxide.

The ratio of carbon monoxide to ethyl formate was found to vary slightly, depending on the amount and kind of ketone present in the reaction mixture. Presumably this discrepancy is due to the condensation of ethyl formate with the ketone according to the Claisen reaction. A concentration of 0.0125 mole of acetone in the reaction so affected the decomposition that only 33.8% of ethyl formate was accounted for. If the concentration was decreased to 0.00085 mole of acetone, which was about that in the samples analyzed in the equilibrium-point determinations, the amount of carbon monoxide formed was 66.6% of the ethyl formate known to be present. This conversion factor was used in calculating the percentage conversion of ketone to acetal. The conversion factors for the other ketones used were obtained by analyses of four or mare samples in which the concentration of ketone was approximately that in the samples of equilibrium mixtures analyzed. These factors ±1.5% were: acetophenone 62.5%; diethyl ketone 63.4%; phenylpropyl ketone 65.2%; methylethyl ketone 66.0%; methylhexyl ketone 65.6%; methyl-*tert.*-butyl ketone 59.4% and benzophenone 66.8%.

TABLE I

SUMMARY OF DATA ON PERCENTAGE CONVERSION OF VARIOUS KETONES INTO ACETALS BY ORTHOFORMIC ESTER

Ketone	Per cent. conversion Retrograde	Synthetic	Ketone	Per cent. conversion Retrograde	Synthetic
$CH_3C{=}OCH_3$	92.62	89.87	$CH_3C{=}OC_6H_5$	67.45	66.87
$CH_3C{=}OC_2H_5$	...	87.73	$C_3H_7C{=}OC_6H_5$	...	64.25
$C_2H_5C{=}OC_2H_5$	86.16	87.49	$C_6H_5C{=}OC_6H_5$	...	31.55
$CH_3C{=}OC_6H_{13}$	85.82	84.91	*tert.*-$C_4H_9C{=}OCH_3$	...	12.48

A summary of the percentage of ethyl orthoformate found as ethyl formate is shown in the table for the synthesis of the acetal of eight ketones and for the retrograde reaction on four of the acetals. An inspection of the values given in the table shows that replacement of one or both of the methyl groups in acetone with higher straight-chain alkyl radicals results in a slight lowering of the percentage conversion to the acetal. A hexyl group has a rather marked effect. The substitution of a phenyl group for a methyl group in acetone lowers the percentage conversion by over 20%, while a second phenyl group causes a further lowering of over 30%. The negative effect of the higher as contrasted with the lower alkyl groups is again shown by the fact that the percentage conversion of phenylpropyl ketone is lower than that of phenylmethyl ketone.

The similarity of the tertiary alkyl radicals to the aryl radicals has been previously noted,[6] but it is surprising to find that methyl tertiary butyl ketone shows a lower conversion than methylphenyl ketone and even lower than diphenyl ketone. The number of ketones for which data are now available is too small to justify any attempt at a theoretical treatment of the subject.'

Preparation and Purification of Reagents

Orthoformic Ester was prepared in the usual way.[8]

Fourteen preparations each involving the use of 250 *g.* of sodium and 400 *g.* of chloroform averaged 375 g. of orthoformic ester boiling at 144–146' at 740 mm. after two fractionations. The 5250 g. of ester so obtained was reduced to 2500 g. by three fractionations through a 20cm. Vigreux column, the product boiling at 145–146° under atmospheric pressure and at 45–46° under 15 mm. This product was further fractionated just before use. The pure ester as used in this work had a density of d_{25}^{25} = 0.9385. The density given in the critical tables[g] is 0.8964.

Ketones.—Acetone was fractionated from a commercial product and purified as by Conant and Kirner;[10] b. p. 56.2–56.7' (740 mm.); $d_{25}^{25} = 0.7964$.

Methylethyl ketone, diethyl ketone, methyl-n-hexyl ketone, acetophenone and phenylpropyl ketone were supplied by the Eastman Kodak Co. Each ketone was dried over anhydrous potassium carbonate and then distilled from a Claisen flask carrying a Vigreux distilling column 20 cm. in length. The products used had the following constants: methylethyl ketone, b. p. 79–81" (760 mm.), & = 0.8072; diethyl ketone, b. p. 101–102" (corr.), sp. gr. 0.8156 (25/25); methyl-n-hexyl ketone, b. p. 173–175" (760 mm.), $d_{25}^{25} = 0.8360$; acetophenone, b. p. 200–202° (760 mm.), $d_{25}^{25} = 1.030$; and phenylpropyl ketone, b. p. 228–229.5° (760 mm.), $d_{25}^{25} = 0.9967$.

Benzophenone was an Eastman Kodak Co. product which had a melting point of 47.5–48°. Methyl-*tert.*-butyl ketone was prepared from pinacol by the pinacoline rearrangement as described in "Organic Syntheses."[11] The boiling point of this product was 103–105° (uncorr.) and its specific gravity was 0.7250(25/25).

Ethyl formate was obtained from the Eastman Kodak Co., and after standing over anhydrous potassium carbonate was freshly distilled before using. The boiling point of this reagent was 54° and its specific gravity was 0.9250 (25/25).

Acetals.—The diethyl acetal of acetone was prepared by a method described by

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[6] Conant and Sloan, THIS JOURNAL, 48, 1743 (1926); Adkins and Adams, *ibid.*, 47, 1368 (1925).

[7] Without further experimental work it does not seem advisable to use these determinations on the amount of ethyl formate formed, for the calculation of the equilibrium constant for the reaction of the orthoformic ester with the ketones, because in some cases it is possible that small amounts of the ethyl formate reacted with ketone according to the Claisen reaction and were therefore not found in the analytical determination. It is anticipated that further work will be done on the extent of the Claisen reaction under the conditions used in this work so that the values given in this paper may be more quantitatively interpreted.

[8] Adkins and McElvain, "Practice of Organic Chemistry," McGraw-Hill Book Co., New York, 1925, p. 80.

[9] "International Critical Tables," Vol. I, p. 215.

[10] Conant and Kirner, THIS JOURNAL, 46, 245 (1924).

[11] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 91.

Claisen,[12] with the exception that 0.0136 g. of dry hydrogen chloride was used as a catalyst in place of 1 g. of ammonium chloride; b. p. (15 mm.) 24–25.5°; d_{25}^{25} = 0.8714.

Diethyl acetal of acetophenone was prepared by the method described by Claisen,[13] with the exception that 0.0136 g. of dry hydrogen chloride was used as a catalyst instead of 0.15 cc. of aqueous hydrochloric acid; b. p. (12 mm.) 110–112°; d_{25}^{25} = 1.0012.

The other diethyl acetals synthesized were prepared in the same manner as was that of acetophenone and possessed the following constants: diethyl acetal of diethyl ketone, b. p. (15 mm.) 51–53', d_{25}^{25} = 0.8810; diethyl acetal of methylethyl ketone, b. p. (16 mm.) 40–41°, d_{25}^{25} = 0.8787; diethyl acetal of methyl-n-hexyl ketone, b. p. (16 mm.) 101–103°, d_{25}^{25} = 0.8798; and diethyl acetal of phenylpropyl ketone, b. p. (15 mm.) 118–120°, d_{25}^{25} = 0.9406.

The preparation of methyl-n-hexyl acetal and phenylpropyl acetal are not described in the literature.

Anal. Calcd. for $(CH_3)(C_6H_{13})C(OC_2H_5)_2$: C, 71.28; H, 12.87. Found: 71.48, 13.11.

Anal. Calcd. for $(C_3H_7)(C_6H_5)C(OC_2H_5)_2$: C, 75.67; H, 9.90. Found: 75.90, 10.12.

Catalyst.—The catalyst used was made up as described by Adkins and Adams,[1] so that a concentration of 0.0136 g. of hydrogen chloride per cubic centimeter of ethyl alcohol was obtained.

Sodium Ethoxide.—Fifty grams of sodium was added to 150 cc. of absolute alcohol in a flask of 500cc. capacity. The flask was connected to a reflux condenser to the top of which was attached a calcium chloride tube. As soon as all of the sodium had reacted, the alcohol was distilled off from an oil-bath in an atmosphere of dry hydrogen. The hydrogen was dried by passing it through concentrated sulfuric acid. The temperature of the sodium ethoxide in the flask was maintained at 180–200° for at least an hour. A pure white product was obtained which turned slightly yellow after a week's time.

Summary

A method has been developed for the quantitative estimation of ethyl formate in the presence of alcohol, orthoformic ester, a ketone and its acetal, which consists in partially converting ethyl formate into carbon monoxide using sodium ethoxide as a catalyst. The percentage of ethyl formate converted into carbon monoxide varied somewhat with the amount and kind of ketone present.

The method of analysis for ethyl formate has been used to determine the extent of the reaction of orthoformic ester with eight ketones: dimethyl, methylethyl, diethyl, methyl-n-hexyl, methylphenyl, phenylpropyl, diphenyl and methyl-*tert.*-butyl ketones. Certain conclusions have been drawn with respect to the relation of the structure of a ketone to the affinity manifested in acetal formation.

The reaction of orthoformic ester with ketones does not proceed in a xylene or toluene solution. The true catalyst would then appear to be a compound of alcohol and hydrogen chloride. Acetophenone reacts much more rapidly than does acetone.

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[12] Claisen, Ber., 40, 3908 (1907).

[13] Ref. 12, p. 3913.

The diethyl acetals of methyl-n-hexyl and phenylpropyl ketones were prepared and analyzed for the first time.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF GEORGETOWN (KENTUCKY) COLLEGE]

ALKYL AMINO-ETHANOL AND PROPANOLS[1]

BY J. STANTON PIERCE

RECEIVED OCTOBER 24, 1927 PUBLISHED JANUARY 5, 1928

Many naturally occurring compounds of therapeutic importance contain the grouping alkyl-N-C-C-0 or alkyl-N-C-C-C-O. Among these compounds are cocaine, quinine, strychnine, hydrastine, hyoscine, atropine and adrenaline. Also, many synthetic medicinals, as procaine, stovaine, alypine, apothesin, butyn and homatropine contain one of these groups.

Since the linkages referred to above are prevalent in so many compounds of marked physiological action, a good method for the preparation of simple substances containing these groupings should be of considerable value in the synthesis of more complex compounds, as those mentioned above. A large number of alkyl amino-ethanols have been prepared by Matthes[2] by the action of ethylene oxide on the monoalkyl amines, but there was usually obtained as by-product the corresponding alkyl dihydroxyethylamine. The latter compounds were difficult to separate from the desired product. A similar method was used by Knorr and Matthes[3] and Knorr and Schmidt.[4] Knorr[5] also condensed aqueous methylamine with ethylene chlorohydrin to form methylamino-ethanol.

This paper deals with the preparation of alkyl amino-ethanol and alkyl aminopropanols by the method used by Otto[6] and Adarns and Segur[7] for aryl amino-ethanols and Pierce with Adams[8] for aryl-aminopropanols. By this method there are no by-products of tertiary amines and in most cases the yield of pure product is fair.

Discussion of Results

The condensation of the alkyl amines with β-chloro-ethylchloroformate and with γ-chloropropylchloroformate took place readily, as was the case

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[1] The author wishes to express his thanks to Professor Roger Adarns, of the University of Illinois, for his valuable suggestions at the outset of this work. Also, acknowledgment is made to the Chemical Department of the University of South Dakota, at which place part of this work was done.

[2] Matthes, Ann., 315, 104 (1901).

[3] Knorr and Matthes, *Ber.*, 31, 1069 (1898).

[4] Knorr and Schmidt, *Ber.*, 31, 1073 (1898).

[5] Knorr, *Ber.*, 22, 2088 (1889).

[6] Otto, *J. prakt. Chem.*, [2] *44*, 15 (1890).

[7] Adams and Segur, THIS JOURNAL, 45, 785 (1923).

[8] Pierce with Adams, *ibid.*, 45, 790 (1923).

of the aryl amines.[7,8] The reaction of β-chloro-ethylallyl carbamate and γ-chloropropylalkyl carbamates with alcoholic potash was much more vigorous than that of the corresponding aromatic compounds. The addition of alcoholic potash to each of the carbamates mentioned in this paper caused the precipitation of potassium chloride and potassium carbonate, indicating the splitting out of hydrochloric acid and carbon dioxide. In all cases the reaction took place without the application of heat and with β-chloro-ethylallyl carbamate the reaction took place almost spontaneously, the heat given off being sufficient to boil the alcohol within a few seconds after the carbamate and potash were mixed.

3-Allyl-2-oxazolidone was obtained by refluxing an alcoholic solution of β-chloro-ethylallyl carbamate with 1.75 moles of potassium hydroxide and vacuum distilling the product. Attempts were made to prepare pure 3-alkyl tetrahydro-1,3,2-oxazones by ring closure of the γ-chloropropyl alkyl carbamates with alcoholic potash and vacuum distilling the products, but constant-boiling products were not obtained.

When the alkyl carbamates mentioned above were refluxed in alcohol solution with 4 moles of potassium hydroxide, no oxazolidone nor oxazones but amino alcohols were isolated. This indicates that, as in the aromatic series,[7,8] these ring nitrogen compounds are decomposed by excess of alcoholic potash. β-Chloro-ethylallyl carbamate yielded β-allylamino-ethanol and the γ-chloropropyl alkyl carbamates yielded the corresponding γ-alkyl amino-propanols.

Experimental Part

β-Chloro-ethyl and γ-Chloropropyl Alkyl Carbamates.—These compounds were prepared by the method described by Pierce with Adams[8] for the preparation of γ-chloropropyl aryl carbamates, sodium carbonate being used as a condensing agent, and the reaction mixtures being kept cool by the addition of ice. As these carbamates are much more soluble in water than the aryl carbamates, the aqueous layers were extracted with ether. The crude carbamates, which were obtained in yields of 84–92%, were purified by vacuum distillation. The yield of pure product was usually about 85% of the crude product. However, for the preparation of the oxazolidone, oxazones and amino alcohols, usually the crude products were used.

All of the carbamates prepared were soluble in alcohol, ether, ethyl acetate, chloroform, carbon disulfide and benzene. In water, β-chloro-ethylallyl carbamate and γ-chloropropylmethyl carbamate were slightly soluble, and the solubility decreased with increase in molecular weight until γ-chloropropylamyl carbamate was practically insoluble.

3-Allyl-2-oxazolidone.—3-Allyl-2-oxazolidone was prepared by refluxing for two hours β-chloro-ethylallyl carbamate, in 2 3 volumes of alcohol, with 1.75 moles of potassium hydroxide. The reaction mixture was cooled, the alcoholic solution decanted from the inorganic residue, the residue extracted with alcohol and the combined alcoholic extract evaporated on a hot-plate at a temperature of 125°. The solution was cooled, filtered into a Ladenburg flask and fractionated *in vacuo*. A very poor yield of pure product was obtained as three fractionations were necessary to separate the ring compound from the amino alcohol and unchanged carbamate present.

The pure product was soluble in water, alcohol, ether, benzene, chloroform, acetone and ethyl acetate, and slightly soluble in carbon disulfide and petroleum ether.

Alkyl Tetrahydro-1,3,2-oxazones.—Several attempts were made to purify by fractional distillation the crude products obtained by refluxing the γ-chloropropyl alkyl carbamates with about 1.5 moles of potassium hydroxide in alcohol. Constant-boiling products were never obtained but the products formed usually had a boiling point, at the pressure used, about 15° above that of the corresponding carbamate. Usually the products had about 0.7% less nitrogen than the pure oxazone would have and they contained a trace of chlorine, indicating the presence of some unchanged carbamate. As it has been shown definitely, in the aromatic series, that 3-aryl tetrahydro-1,3,2-oxazones are intermediates[S] in the preparation of arylaminopropanols, from the corresponding y-chloropropyl aryl carbamates, the high-boiling products referred to above are doubtless 3-alkyl tetrahydro-1,3,2-oxazones.

β-Allylamino-ethanol and γ-Alkyl Aminopropanols.—Allylamino-ethanol and the alkyl aminopropanols were prepared as were the corresponding aryl amino-ethanols[7] and propanols.[8] However, due to the greater solubilities of the alkyl compounds, the method of isolation and purification was modified somewhat.

Two methods were used for the isolation of allylamino-ethanol and the alkyl aminopropanols. In one method potassium carbonate was added in considerable excess to the alcoholic solution of the amino alcohol and, after the mixture had stood for two hours, the solution was filtered, the alcohol evaporated and the residual liquid vacuum distilled. The other method consisted of steam distilling the reaction mixture, acidifying the distillate, evaporating to low volume, neutralizing the acid with sodium hydroxide, salting out the amino alcohol with potassium carbonate and vacuum distilling the prod-

TABLE I

COMPOUNDS PREPARED, YIELDS, CONSTANTS AND ANALYSES

						Analysis			
Compound	Formula	Yield, % crude	B. p.	d_4^{20}	Index of ref.	Wt., g.	N_2, cc.	% Calcd., %	% Found, %
β-Chloro-ethyl allyl carbamate	$C_6H_{10}O_2NCl$	92	103.5–104.5° (1.3 mm.)	1.1811	N_D^{27} 1.4668	0.2018	16.2, 29°, 740 mm.	8.6	8.5
γ-Chloropropyl allyl carbamate	$C_7H_{12}O_2NCl$	91	110–111° (1 mm.)	1.1390	N_D^{26} 1.4681	.1762	13.2, 26°, 738 mm.	7.9	8.0
γ-Chloropropyl methyl carbamate	$C_5H_{10}O_2NCl$	84	104.5–106° (1 mm.)	1.1821	N_D^{27} 1.4548	.1886	16.7, 28°, 742 mm.	9.2	9.4
γ-Chloropropyl n-amyl carbamate	$C_9H_{18}O_2NCl$	88	135–137° (2 mm.)	1.0629	N_D^{21} 1.4560	.2070	13.2, 27°, 735 mm.	6.7	6.8
		(Purified)							
3-Allyl-2 oxazolidone	$C_6H_9O_2N$	21	123–125° (0.7 mm.)	1.113	N_D^{27} 1.4691	.1335	14.1, 30°, 738 mm.	11.0	11.1
β-Allylamino ethanol	$C_5H_{11}ON$	48	77–80° (1.5 mm.)	0.9398	N_D^{27} 1.4602	.1584	20.5, 24°, 736 mm.	13.9	14.0
γ-Allylamino propanol	$C_6H_{13}ON$	48	88–90' (0.8 mm.)	,9319	N_D^{27} 1 4629	.1280	14.6, 23°, 738 mm.	12.2	12.4
γ-Methylamino propanol	$C_4H_{11}ON$	31	74–77° (2.5 mm.)	.9315	N_D^{27} 1 4418	.1308	19.1, 22°, 731 mm.	15.7	15.8
γ-*n*-Amylamino propanol	$C_8H_{19}ON$	47	103–105" (1.8 mm.)	.8858	N_D^{21} 1.4493	.1628	14.8, 30°, 739 mm.	9.6	9.5

uct. The latter method worked very well with γ-allylaminopropanol and γ-amylaminopropanol but was not very good for γ-methylaminopropanol and β-allylamino-ethanol, due to their great solubility in water. In all cases better yields would be obtained by working with larger amounts.

All of the amino alcohols were colorless liquids when freshly prepared but darkened on standing. All had a characteristic odor. All were soluble in water, alcohol, ether, chloroform, ethyl acetate and acetone. The solubility in water decreased with increase in molecular weight, for, although all dissolved readily, amylaminopropanol was salted out readily with potassium carbonate, allylaminopropanol was salted out a little less readily and methylaminopropanol and allylamino-ethanol could scarcely be salted out. In carbon disulfide and petroleum ether amylaminopropanol was readily soluble, while the lower molecular weight amino alcohols went into solution with difficulty.

Summary

1. Allylamine was condensed with β-chloro-ethylchloroformate to yield β-chloro-ethylallyl carbamate. The latter compound, refluxed with 1.5 moles of alcoholic potash, yielded 3-allyl-2-oxazolidone, and with 4 moles of alcoholic potash, yielded β-allylamino-ethanol.
2. Allyl-, methyl-, and n-amylamines condensed with γ-chloropropylchloroformate to yield the corresponding γ-chloropropyl alkyl carbamates. These carbamates, refluxed with 4 moles of alcoholic potash, yielded the corresponding γ-alkyl aminopropanols.

GEORGETOWN, KENTUCKY

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 156]

THE PREPARATION OF 2-BROMO-*p*-CRESOL FROM p-NITROTOLUENE

BY HOWARD J. LUCAS AND NATHAN F. SCUDDER

RECEIVED OCTOBER 26, 1927 PUBLISHED JANUARY 5, 1928

The usefulness of 2-bromo-p-cresol in standardizing bromide-bromate solutions[1] makes desirable a convenient method of preparation. It has been obtained from 2-amino-*p*-cresol through the diazo reaction[2] and its use as a dye intermediate has been suggested.[3]

In this work it has been found that the desired compound may be conveniently obtained in satisfactory yield from *p*-nitrotoluene by the following operations.

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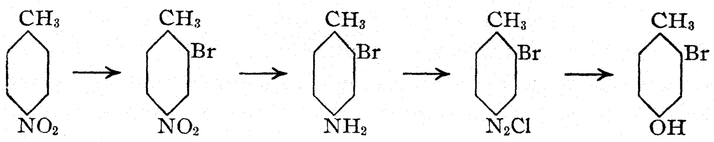
[1] Buxton and Lucas, THIS JOURNAL, 50, 249 (1928).

[2] Plummer, Melamed and Puttfarchen, Ber., **55B,** 3116 (1922).

[3] D. R. P. 156,333; *Chem.* Cent., **1904,** II, 1673.



Bromination of p-Nitrotoluene

In the usual method of brominating p-nitrotoluene[4] the materials, including iron bromide, are sealed in a tube and heated to 170° We have found that, using iron filings as the source of the iron bromide, the reaction proceeds with moderate rapidity at 50–60° and, although some bromine is lost in the process, the yield obtained is satisfactory.

To 300 g. (2.2 moles) of p-nitrotoluene (Eastman) and 10 g. of iron filings in a flask fitted with a return cooler is slowly added 370 g. (2.3 moles) of cold bromine. The flask is surrounded by an ice-bath in order to moderate the reaction, which is quite rapid at first and continues vigorously for about one hour. The next day it is slowly heated by means of a warm water-bath and finally to 150° by means of an oil-bath until the evolution of hydrogen bromide ceases. This requires about three hours.

The mass, after cooling, is shaken with an aqueous solution of sodium bisulfite, in order to remove hydrogen bromide and unchanged bromine, and then leached out with cold alcohol in order to remove any unchanged nitrotoluene. Crystallization from hot alcohol gave 358 g. of 2-bromo-4-nitrotoluene (76% yield). Although the yield is lower than that obtained by Scheufelen,[4] the superiority of this method lies in the greater convenience and saving of time.[5]

Reduction of 2-Bromo-4-Nitrotoluene

Although 2-bromo-4-aminotoluene has been prepared in other ways,[5,6] the reduction of the corresponding nitro compound seems to be the most practicable. Neville and Winther[7] reduced with tin and hydrochloric acid, while Blanksma[5] reduced with sodium bisulfide in alcohol solution, obtaining not only the expected bromotoluidine but also 2-bromo-4-aminobenzaldehyde. In this work ammonium sulfide in alcohol was used as the reducing agent and gave a satisfactory yield (85%) of the expected amine, which was easily purified from a small amount of another substance which may have been the compound observed by Blanksma. The following method was employed. An alcoholic solution of ammonium sulfide was prepared by passing anhydrous ammonia into 1 liter of alcohol until the gain in weight was 108 g. (6.35 moles), followed by hydrogen sulfide until no more was absorbed, 90 g. (2.65 moles). When about half of the hydrogen sulfide had been added, white plate-like crystals came

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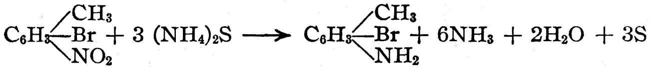
[4] Scheufelen, *Ann.*, 231, 171 (1885); Cohen and Dutt, J. *Chem. Soc.*, 105, 505 (1914); a 94% yield is claimed.

[5] The desired compound may also be obtained from 2-amino-4-nitrotoluene by the Sandmeyer method, Blanksma, *Chem. Weekblad,* 6, 899 (1909).

[6] Hafner, *Ber.*, **22,** 2903 (1899), obtained 2-bromo-4-aminotoluene along with some of the 3-isomer by brominating the sulfate of p-toluidine.

[7] Neville and Winther, *ibid.*, 14, 418 (1891). No yield is given.

down and by the time saturation was reached the mixture had become mushy due to the separation of ammonium sulfide. The amount of 2-bromo-4-nitrotoluene, 150 g. (0.66 mole), was so chosen that there would be about 30% excess[8] of ammonium sulfide needed for the reduction according to the equation



$$C_6H_3\begin{cases}CH_3\\ Br\\ NO_2\end{cases} + 3\ (NH_4)_2S \longrightarrow C_6H_3\begin{cases}CH_3\\ Br\\ NH_2\end{cases} + 6NH_3 + 2H_2O + 3S$$

The unchanged ammonium sulfide (30%) would react with the sulfur to form the poly-sulfide, as follows

$$(NH_4)_2S + 3S \longrightarrow (NH_4)_2S_4$$

The characteristic brown color of the polysulfide which develops as the operation proceeds is useful in indicating the extent of the reaction. Soon after mixing there was a small heating effect which was taken care of by placing the flask in an ice-bath. At first the color of the solution was unaffected but later on it changed rapidly from yellow to red-brown. After standing overnight the flask was heated on a steam-bath under a reflux condenser in order to drive out the ammonium sulfide, which was absorbed by another portion of alcohol preparatory for a subsequent run. By passing a slow stream of air through the system the troublesome condensation of solid ammonium sulfide in the condenser could be avoided. After heating for some hours, the ammonium sulfide was largely removed from the alcoholic liquid, which had lost all but a trace of the brown color and was mixed with much precipitated sulfur. The liquid was filtered hot to remove sulfur and then the alcohol was evaporated on the steam-bath to small volume, leaving a brown oil.[9] The oil was heated with sufficient 6 N hydrochloric acid to dissolve it hot; the resulting solution was filtered from a small amount of sulfur and allowed to cool. Long, slender crystals having a pale brown tint separated, weight 130 g. Evaporation of the filtrate to small volume and cooling gave a small amount of yellow amorphous solid but no crystals. The yield of the hydrochloride of 2-bromo-4-aminotoluene is 84%.

This salt was obtained in fine, snow-white needles by crystallizing 25 g. from hot absolute alcohol (300 cc.) in which dry hydrogen chloride was dissolved. After washing with absolute alcohol, the crystals were dried for thirty-six hours in a vacuum desiccator containing both concentrated sulfuric acid and solid sodium hydroxide. Two analyses for chloride ion by precipitation as silver chloride gave 15.95 and 15.97%; the theoretical is 15.94%. The melting point in a sealed tube was 271°.

Treatment of the purified salt with concentrated ammonium hydroxide

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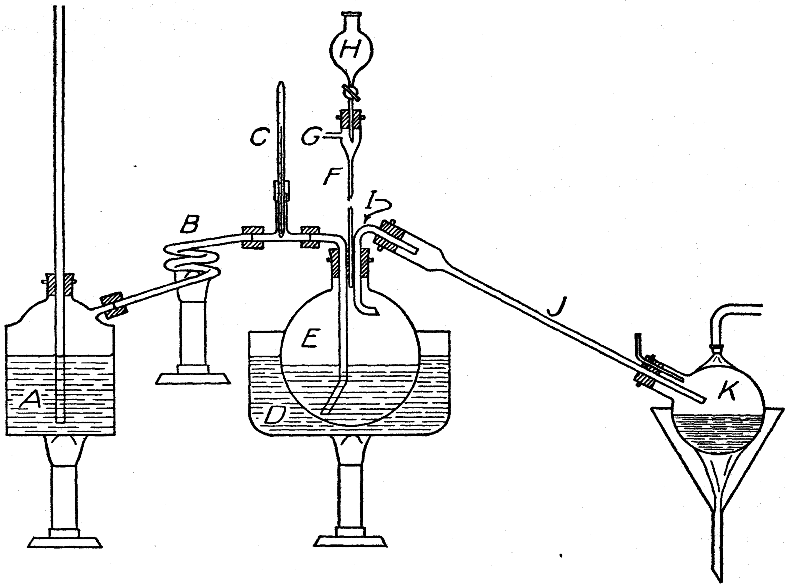
[8] With 100% excess of ammonium sulfide the yield was much lower (56%).

[9] A more convenient method of working up the reaction mixture would consist in distilling off alcohol and ammonium sulfide together, leaving behind the crude amine.

gave the free base, which after drying over solid sodium hydroxide was slightly brown in color and melted at 27.3–27.5° (corr.).

2-Bromo-p-Cresol from the Amine

Attempts to convert the amine into the corresponding hydroxyl compound by the usual method of heating the diazotized solution of the amine led to the formation of much tar, from which only small amounts of the cresol could be extracted. However, by heating the diazo solution rapidly and distilling out the product as soon as it formed, a satisfactory yield was obtained. This was accomplished in the apparatus shown in the figure by the following method. The hydrochloride of the amine, 90 g. (0.4 mole), was dissolved in a hot solution of 55 cc. of concentrated hydrochloric acid and 350 cc. of water. This was cooled to 2–3° and diazotized with a solution of 31 g. of sodium nitrate (5% excess) in 120 cc. of water in the usual way. To the diazotized solution, now about 500 cc., was added 150 cc. of cold, dilute sulfuric acid (approximately 65%, from equal volumes of acid and water), keeping the temperature at all times below 8°. This cold, diazotized solution was placed in the dropping funnel H, and introduced rapidly in portions of 10–15 cc. into the flask



A, Steam generator; B, steam heater; C, thermometer; D, oil-bath, 130–140°; E, balloon flask, 3 liter; F, tube, internal diameter 2 mm., length 30–40 cm.; G, side arm for compressed air; H, container for diazotized amine; I, exit tube, internal diameter 10–12 mm.; J, condenser tube, length 60 cm.; K, flask, 2 liter, cooled by water.

Fig. 1.—Apparatus for converting diazotized bromotoluidine into bromocresol.

E which contained a hot mixture of 750 g. of anhydrous sodium sulfate, 300 cc. of concentrated sulfuric acid and 300 cc. of 6 N sulfuric acid,[10] and was heated by the oil-bath D kept at 130–140°. Steam heated to 160–180° in the heating coil B was passed into the flask, thus removing the cresol as soon as it formed and preventing a coupling reaction between it and the diazonium salt.

By adding the diazo solution rapidly and blowing off the last few drops from the tube F by a jet of air through G, it cannot become warm and undergo reaction before it enters the flask. The distillate of approximately 600 cc. was shaken twice with about 200 cc. of benzene and the benzene solution then extracted with 1000 cc. of 2 N sodium hydroxide. The alkaline solution after filtering and acidifying with sulfuric acid gave an oil which solidified in the ice box overnight. The crude 2-bromo-*p*-cresol was filtered off and after drying in a vacuum desiccator over sulfuric acid weighed 91 g. (yield, 80.5%).

The bromocresol was purified by washing with some cold redistilled petroleum ether, b. p. 40–63°, to remove most of the colored impurity, and then crystallized from another portion, b. p. 40–75°, giving white, silky, slender needles. Since the temperature coefficient of solubility is high, slow cooling was necessary in order to avoid excessive supersaturation and the formation of a liquid instead of the desired solid phase. The first crop when dissolved in petroleum ether gave an almost colorless solution and crystallized out as before. The recrystallized material melted at 55.2–55.4° (corr.) to a colorless liquid.[11] By proper evaporation of the filtrate the greater part of the 2-bromo-*p*-cresol is recovered. Thus from a total of 142 g. of crude material there was obtained 131 g. (92% recovery) of the purified cresol. On this basis the best yield of purified 2-bromo-*p*-cresol calculated back to nitrotoluene is 47% for the three operations, whereas that obtained by Plummer[2] from 2-amino-*p*-cresol through the diazo reaction in one operation was 18.5%.

Analyzed for bromine by the Carius method, 0.2031 g. of 2-bromo-*p*-cresol gave 0.2066 g. of AgBr, and 0.2447 g. gave 0.2457 g. of AgBr, equivalent to 43.3 and 42.7% of bromine, compared to the calculated value of 42.7%.

The cresol is exceedingly soluble in benzene and in methyl, ethyl and propyl alcohols and does not crystallize readily from these solvents. It is readily soluble in ligroin, from which it separates as a liquid phase. Petroleum ether, b. p. 40–75°, is the most satisfactory solvent for purification purposes.

The Benzoate of 2-bromo-*p*-cresol.—This compound was easily obtained from the cresol by the Schotten-Baumann reaction. After treatment with sodium hydroxide solution, followed by two crystallizations from absolute alcohol, it separates in the form of large, white needles melting at 74.6–75.1° (corr.), a value unchanged by further crystallization.

Summary

Starting with *p*-nitrotoluene, 2-bromo-*p*-cresol has been obtained in yields of 47% by the operations of bromination, reduction and replacement of the diazonium group.

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[10] A mixture of this composition, which is in reality largely sodium acid sulfate with smaller amounts of sulfuric acid and water, has a boiling point of 135°.

[11] Previous observers, Plummer, ref. 2, gave 54–55°, and D. R. P., ref. 3, 55–56°.

Replacement of the diazonium group by hydroxyl is best accomplished by running the diazotized amine into a solution of sulfuric acid and sodium sulfate at 130–140°, and continually distilling out the cresol with superheated steam.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 157]

THE ANALYSIS OF BROMINATED CRESOLS

BY JOHN BUXTON AND HOWARD J. LUCAS

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Previously described methods which were being employed for analyzing mixtures of brominated cresols were found to be troublesome enough to justify further investigation in the hope that improvements could be made. In the bromide-bromate titration method of Francis and Hill[1] there is, after acidification, a slow reaction between the standard solution and the alcohol used as solvent. In the method of halogen determination proposed by Robertson[2] the end-point of the final titration is difficult to determine because hydrogen peroxide present in the solution reacts with the thiocyanate.

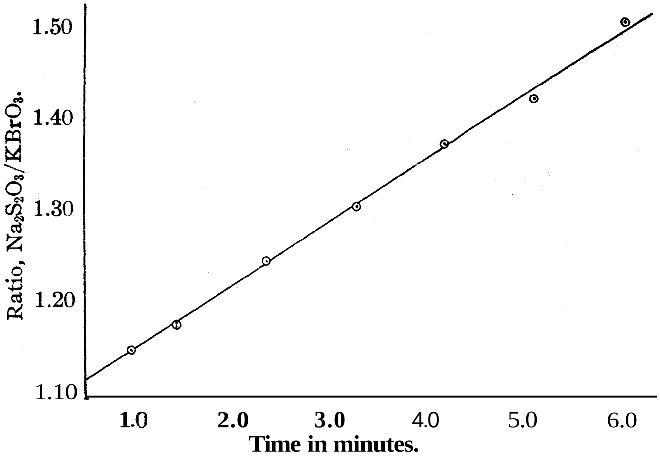

Fig. 1.—Effect of alcohol upon standard bromate solution in 1 N H_2SO_4.

The Bromide-Bromate Titration.—In the method of Francis and Hill it was found that the reaction between alcohol and bromate in acid solution decreased the amount of thiosulfate required for back titrations. Fig. 1 shows how the ratio of 0.1005 N thiosulfate to 0.091 N bromate changes

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[1] Francis and Hill, THIS JOURNAL, 46, 2499 (1924).

[2] Robertson, J. Chem. *Soc.*, 107, 902 (1912).

with time when 15.00 cc. of standard bromide-bromate solution stands with 50 cc. of water, 15 cc. of alcohol and 5 cc. of 18 *N* sulfuric acid. This reaction may not ordinarily be bothersome in the procedure recommended by Francis and Hill since the solution is not made acid until all of the bromate is introduced. However, any variations in time, temperature or concentration from the standard conditions might introduce errors. It has been found that by substituting glacial acetic acid for alcohol the undesirable side reaction between the solvent and the bromate solution is eliminated.

The following is the method finally adopted: approximately 0.10 to 0.15 g. of the phenol or substituted phenol is dissolved in 25 cc. of glacial acetic acid in a glass-stoppered conical flask and diluted with 50 cc. of water. Standard bromide-bromate solution of about 0.1 normality is introduced slowly until there is an excess of 2 to 4 cc., as shown by the development of the bromine color. This liberation of free bromine when the bromate is in excess is a convenience since it is not necessary to know in advance the bromine requirement of the sample. The solution is shaken thoroughly and allowed to stand for about one minute, at which time approximately 0.5 g. of potassium iodide is added and the liberated iodine is titrated with standard thiosulfate. The method was checked against pure 2-bromo-*p*-cresol, m. p. 55.2–55.4,[3] with the following results.

Wt. of 2-bromo-*p*-cresol taken, g.	Cc. of 0.100 N bromate	Wt. found, g.	Percentage error
0.1254	26.79	0.1252	0.16
.1698	36.03	.1684	.82

A sample of 3-bromo-p-cresol which distilled at 104–105.5' under 20 mm. on a second distillation gave the following results on analysis.

Wt. of sample taken, g.	Cc. of 0.0986 N bromate	Wt. found, g.	Percentage error
0.1715	18.68	0.1721	0.35
.2047	22.10	.2037	.49

Mixtures of known amounts of 2-bromo- and 3-bromo-p-cresol gave

Wt. of 2-bromo-, g.	Wt. of 3-bromo-, g.	Cc. of 0.0986 N bromate	% of 3-bromo-	
			Present	Found
0.0317	0.1732	26.02	84.5	83.0
.0253	.2188	28.98	89.6	90.6
.1018	.1683	40.14	62.3	63.0

The per cent. of each isomer was calculated according to the following equations

$$x = \frac{9.35\,nc}{w} - 100 \quad \text{and } y = 200 - \frac{9.35\,nc}{w}$$

where x and y are the per cent. of 2-bromo and 3-bromo-p-cresol, respectively, w = weight of sample, *n* = normality of the bromate solution

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[3] Lucas and Scudder, THIS JOURNAL, 50, 244 (1928).

and c = number of cc. used. Since 2-bromo-*p*-cresol may be obtained quite pure by the method described elsewhere[3] its use as a means of standardizing the bromide-bromate solution is here suggested.

The Determination of Total Bromine.—In Robertson's[2] method of halogen determination the end-point of ferric thiocyanate fades rapidly due to the presence of hydrogen peroxide. To one who has developed considerable familiarity with the titration the fading may not be bothersome, but to one who is using the method for a short time only this complication may give much trouble. The removal of the hydrogen peroxide may be accomplished by boiling the solution while still alkaline with some of the iron salt which is needed for the end-point, for under these conditions the peroxide decomposes completely. If more than 1 cc. of 1 N ferric nitrate solution is added before boiling, the ferric hydroxide dissolves very slowly after acidifying.

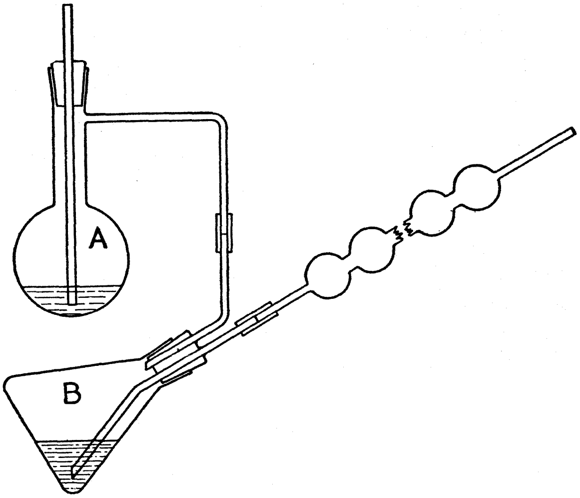

Fig. 2.—Absorption apparatus for bromine determination.

The apparatus of Robertson, Pig. 2, was modified for the sake of convenience by building it in separate units which could be joined together by heavy pieces of rubber tubing well lubricated with sirupy phosphoric acid. The modified method follows: sufficient sample to give the equivalent of 9 cc. of 0.1 *N* silver nitrate is weighed into the reaction flask A and covered with 30 cc. of cold concentrated sulfuric acid which should be free from chloride. The acid is added by means of a funnel while the flask is kept surrounded by an ice-salt bath. After the sample has dissolved and the temperature of the contents has dropped to zero, 10 g. of c. p. chromic anhydride is added and the connection is made to the absorption flask B, which should contain 40 cc. of 1 *N* sodium hydroxide and

20 cc. of 3% hydrogen peroxide, both free of halides. Heat is applied slowly to flask A, care being taken not to increase the temperature rapidly, otherwise the reaction may become too vigorous and lead to the production of smoke, the presence of which should be avoided since low results invariably accompany it. After the end of the reaction, which usually requires about forty-five minutes, a slow stream of air is passed through the apparatus in order to sweep the vapors of bromine and hydrogen bromide over into the absorption apparatus and at the same time the mixture is heated more strongly so as to decompose most of the excess chromic acid. After about fifteen minutes longer the apparatus is disconnected, the solution is washed out of the absorption tube into the flask and 1 cc. of 1 N ferric nitrate is added to the solution. It is boiled for ten minutes in order to decompose the hydrogen peroxide and after cooling is acidified with 20 cc. of 6 *N* nitric acid. In order to have a good end-point, 9 cc. more of ferric nitrate is added. The titration is made by adding 10 cc. of 0.1 N silver nitrate, filtering, washing the precipitate and back titrating the filtrate and washings with 0.1 N potassium thiocyanate.

The reliability of the method is indicated by the results obtained with a pure specimen of 2-bromo-*p*-cresol,[3] for which the bromine content was found to be 42.95 and 43.02%, compared to the calculated value of 42.50%.

Summary

The bromide-bromate titration method of Francis and Hill as applied to brominated cresols is best carried out in water-acetic acid solution.

A procedure has been suggested for obtaining a better end-point when determining bromine in brominated cresols by the method of Robertson.

PASADENA, CALIFORNIA

NOTE

Improved Lighting Source for Melting-Point Apparatus.—A melting point determination, when taken on a dull day or at night under artificial light, is both difficult to accomplish and a strain on the eyes. If a light is placed directly above or behind the melting-point apparatus, considerable reflection from the glass surface results, and the intensity of light directed at the melting point tube is very small. In order to avoid these obstacles, a simple device has been developed.

A short length of tube or rod of any clear glass, fused quartz being desirable but not essential, will transmit practically the entire intensity of light with very little loss of light transversely, and this property is utilized in an apparatus constructed as follows. A small box built of aluminum, or of wood lined with tin foil, holds an electric light bulb (about 100 watts). In the wall opposite the bulb is a hole through which a piece of quartz tube, 8 mm. in diameter and 4 cm. long, is projected. This box is placed so that the beam of intense light coming through the end of the quartz tube projects on the material in the melting point tube, allowing the observer to follow the fusion of the substance easily, with the added advantage that none of the light is directed at the observer's eyes. To prevent overheating it is preferable to provide breathing holes in the bottom and top of the box.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMICAL ENGINEERING,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS
E. V. FASCE

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NEW BOOKS

Kolloidchemie: Ein Lehrbuch. (Colloid Chemistry: A Textbook.) BY DR. RICHARD ZSIGMONDY, Professor at the University of Göttingen. II. Fifth, enlarged and completely revised edition. Otto Spamer, Leipzig, Germany. 1927. x + 256 pp. 16 figs. 25 × 17.5 cm. Price, unbound, Rm. 14; bound, Rm. 16.

The author speaks of this book as a textbook. It is really more of a handbook; particularly this second volume, in which the author takes up *seriatim* all the various colloids which have been prepared and studied. The inorganic colloids occupy about two-thirds, the organic colloids about one-third of the volume.

Under each colloid are given the methods used for its preparation, its properties and behavior, its occurrence and uses. The volume affords a valuable and, so far as I know, unique handbook of what might be called descriptive colloid chemistry.

The treatment is clear and succinct. However, references to the earlier editions are perplexingly numerous so that one really needs to have them at hand.

Professor Handovsky and Dr. Thiessen, both of the University of Göttingen, wrote the chapters entitled, respectively, "Colloidal Albumins" and "Soaps."

ARTHUR B. LAMB

An Introduction to Organic Chemistry. By ROGER J. WILLIAMS, Ph.D., Associate Professor of Chemistry, University of Oregon. D. Van Nostrand Company, Inc., 8 Warren Street, New York City, 1927. ix + 565 pp. 8 figs. 22 X 14 cm. Price, $3.75.

The author has been refreshingly successful in his attempt to bring organic chemistry into consonance with the modern treatment of descriptive inorganic chemistry which precedes it in the student's course of study. The selection of descriptive material and the order of its presentation obviates reference to pages further on in the story whose subject matter as a whole has not been studied and excerpts from which are so often misunderstood or entirely misleading. Infractions of this rule occur so late in the text that they are not so annoying and harmful. Some consideration of atomic structure in a textbook for beginners was long overdue. However, the appearance in such a book of equations showing the production of oxygen and hydrogen available for oxidation or reduction processes might well be a subject for adverse criticism.

The attentive student of this text will be ever mindful that the criterion of the soundness of theory is its conformation to facts. In its pages he will find sound treatment of fundamentals and enough illustrative application of them to inspire him to further study of larger works and literature.

Perhaps a little too exhaustive consideration is given to the proteins, but on the whole the book is well balanced. It is handy in form and attractive in appearance. Without question it shows distinct progress from a pedagogical standpoint and merits most careful consideration.

C. E. BOLSER

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. VII. Edited by FRANK C. WHITMORE, WITH ROGER ADAMS, H. T. CLARKE, J. B. CONANT, HENRY GILMAN AND C. S. MARVEL. John Wiley and Sons, Inc., 440 Fourth Avenue, New York City, 1927. 105 pp. 1 fig. 23.5 X 15.5 cm. Price $1.50.

The seventh volume of Organic Syntheses is at hand, with a new Editor-in-Chief but with the same Editorial Board, and without any change in the essential features of earlier volumes. The reviewer notes with pleasure that nearly all of the thirty preparations have been supplied by contributors, of whom more than half appear for the first time in this volume. Since the editorial board, on principle, assumes the burden of checking all directions, we others have no better way of showing our gratitude for this large and steadily increasing number of carefully developed preparations than by contributing our bit.

The present volume contains directions for the following preparations: anhydro-2-hydroxymercuri-3-nitrobenzoic acid, *p*-arsonophenoxyacetic acid, benzanilide, β-bromo-ethylphthalimide, 2-bromo-3-nitrobenzoic acid, chloro-acetamide, *p*-chloromercuribenzoic acid, α-cyano-β-phenylacrylic acid, p-dimethylaminobenzophenone, 3,5-dinitro-anisole, diphenic acid, ethyl bromomalonate, ethyl n-butylacetoacetate, furan, furfuralacetone, 2-furylmethyl acetate, guanidine nitrate, hydrogen cyanide (anhydrous), β-hydroxypropionic acid, β-iodobenzoic acid, methyl n-amyl ketone, α-methyl mannoside, nitroguanidine, 3-nitrophthalic acid, 3-nitrophthalic anhydride, pentene-2, phthalimidomalonic ester, triphenyl stibine, xanthone, xanthydrol.

E. P. KOHLER

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

OBSERVATIONS ON THE RARE EARTHS. XXV. EXAMINATION OF CERTAIN RARE EARTH MATERIALS FOR ELEMENT NUMBER 72

BY WILLIAM B. HOLTON[1] WITH B. S. HOPKINS

RECEIVED FEBRUARY 10, 1927 PUBLISHED FEBRUARY 4, 1928

Considerable interest has attached to the question of the possible presence of element number 72 in rare earth minerals, and especially in the more soluble fractions of the yttrium group, because of the assertion of Urbain that the element celtium was found in such material. This investigation was undertaken for the purpose of furnishing more information pertaining to this interesting question.

Inasmuch as both zirconium and thorium, the two most closely related homologs of element number 72, are often found in varying percentages in rare earth minerals, it seems reasonable to suppose that element number 72, which comes between zirconium and thorium, should likewise be present. It is a well-known fact that the usual procedures employed for the separation of the rare earths concentrate the thorium and zirconium content in the most soluble fractions of the series. Wherefore, it is not improbable that element number 72 might also be present in these same fractions.

X-Ray Analysis

With this possibility in mind, an x-ray analysis[2] was made of the oxide material prepared from the most soluble fractions of two different crystallization series of the yttrium group. The L-series spectra in the region of the $L\alpha_1\alpha_2$ doublet for element number 72 was photographed but the most intense $L\alpha_1$ line was not visible on the plates. This would indicate that if this element were present, its concentration must be less than one part in one thousand, which we believe is the limiting concentration detectable by our method of x-ray analysis.

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[1] An abstract of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

[2] Harris, Yntema and Hopkins, THIS JOURNAL, 48, 1594 (1926).

Arc Spectrum Analysis

The arc spectrum lines in the ultraviolet region are already well known for element number 72.[3] Using an E-1 model Hilger quartz prism spectrograph, we have measured the wave lengths of twenty-five of the most prominent and easily recognized lines of this element in order that they may be used for comparison. These selected lines are free from coincidence with all but a very few of the minor arc spectrum lines of the rare earths, zirconium, thorium and other probable interfering elements.[4] The material used to obtain this arc spectrogram was a mixture of the oxides of zirconium and element number 72, containing approximately 30% of the latter element.[5]

The wave lengths which we measured and the intensities as we observed them are given in the first column of the accompanying table, while the corresponding values as noted by Hansen and Werner are listed in the second column.

The arc spectrograms of eight rare earth preparations were examined, not only for these lines of element number 72, but also for the major lines of both zirconium and thorium. The first, second, third and fourth preparations were materials obtained at various steps in the working up of some original gadolinite from Hittero, Norway. The presence of most of the rare earth elements and thorium was readily established. No evidence was obtained for the presence of either zirconium or element number 72.

The fifth and sixth preparations were phosphate precipitates obtained from the soluble end fractions of the two yttrium group series which were used in the x-ray analysis. The seventh preparation was a similar precipitate obtained from the soluble end fractions of a cerium group series. In these three materials thorium was found present but the presence of zirconium and element number 72 could not be established.

Preparation No. 8 was a solution of nitrates obtained from some potassium double sulfate residues. This rare earth–potassium double sulfate residue was the accumulation of many years' work, obtained by treating the most soluble fractions of various yttrium group series with potassium sulfate to remove the cerium elements along with zirconium and thorium. The arc spectrogram of this material revealed the presence of much thorium and no zirconium. The evidence with regard to element number 72 is presented in the third column of the accompanying table. The intensity symbols used in this connection have the following meanings: ab—absent; 0—a faint, yet distinctly perceptible line; and the other

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[3] Hansen and Werner, Nature, **112**, 618–619 (1923).

[4] For the arc spectrum lines of these elements, see H. Kayser, "Handbuch der Spectroscopie," Hirzel, Leipzig, 1908–1912, Vols. IV, V and VI.

[5] This material was given to us by Dr. F. H. Driggs of this Laboratory.

numbers indicate proportionally increasing intensity. We feel that the probable presence of element number 72 is indicated in this material.

TABLE I

WAVE LENGTHS OF THE MOST READILY DISTINGUISHABLE LINES IN THE ARC SPECTRUM OF ELEMENT NUMBER 72

Holton and Hopkins		Hansen and Werner		Potassium double sulfate residues	
3428.37	1	3428.39	5	3428.37	ab
3417.33	1	3417.36	5	3417.33	ab
3352.03	2 (Ti)	3352.03	6 (Ti)	3352.03	0
3332.73	2	3332.74	6	3332.73	1
3312.88	1	3312.86	6	3312.88	ab
3253.71	2	3253.70	6	3253.71	0
3194.21	2	3194.20	6	3194.21	1
3176.83	2	3176.86	6	3176.83	0
3134.73	2	3134.77	6	3134.73	ab
3109.12	2	3109.14	6	3109.12	ab
3101.34	1	3101.42	6	3101.34	1
3080.66	1	3080.77	6	3080.66	ab
3072.92	6 (Ti)	3072.94	6	3072.92	1
3067.35	2	3067.39	6	3067.35	ab
3057.07	3	3057.04	5	3057.07	0
3016.79	4	3016.77	6	3016.79	ab
3000.07	1	3000.12	5	3000.07	ab
2982.70	1	2982.74	5	2982.70	0
2950.69	2	2950.72	5	2950.69	ab
2929.64	2	2929.66	5	2929.64	0
2919.61	2	2919.61	6	2919.61	0
2909.94	1	2909.91	5	2909.94	0
2898.70	2	2898.79	5	2898.70	0
2898.23	3	2898.31	6	2898.25	1
2866.37	5	2866.37	5	2866.37	1
2861.68	4	2861.72	6	2861.68	1
2861.04	4	2861.04	6	2861.04	0
2773.39	4	2773.42	6	2773.39	0

Summary

1. The method of x-ray analysis failed to show the presence of element number 72 in the most soluble fractions of rare earth elements of the yttrium group.

2. Arc spectrum analysis showed the presence of thorium and failed to show the presence of zirconium (1) in gadolinite from Hitterö, Norway, (2) in the most soluble fractions of rare earth elements from both the yttrium and cerium groups, **(3)** in an accumulation of potassium double sulfate residues obtained from the soluble end fractions of various yttrium group series.

3. Arc spectrum analysis failed to show the presence of element number 72 in any of the aforementioned rare earth materials except the last.

4. Arc spectrum analysis indicated the probable presence of element number. 72 in the potassium double sulfate residues from the yttrium group.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. III
THIOHYDROLYSIS OF CHLORIDES[1]

BY A. W. RALSTON AND J. A. WILKINSON

RECEIVED APRIL 14, 1927 PUBLISHED FEBRUARY 4, 1928

In the two previous papers from this Laboratory concerning liquid hydrogen sulfide as a reaction medium[2,3] it has been shown that while liquid hydrogen sulfide has, in many ways, more the properties of an organic solvent than water has, nevertheless there are some reactions that bring out its close relationship with water. One of these is its reaction with chlorides, especially those of the elements of the fifth group in the periodic table. This reaction, which corresponds to hydrolysis in water systems and ammonolysis in ammonia systems, has been designated as thiohydrolysis. While the above mentioned chlorides are the most reactive, other chlorides have been studied in order to make the series complete.

Most of the truly metallic chlorides, except $AlCl_3$, $FeCl_3$, $HgCl_2$ and $ZnCl_2$, are quite insoluble and non-reactive, but the more non-metallic chlorides are not only very soluble but many of them are quite reactive. An attempt has been made to bring about these reactions and to examine the products formed to show how complete is the thiohydrolysis.

Experimental

The liquid hydrogen sulfide was prepared in an apparatus very similar to that used by Quam.[2] The chlorides, after careful purification, were placed in heavy-walled, well-annealed glass tubes of about 10cc. capacity which had been dried by washing with alcohol and ether and then heating in an oven while passing a current of dry air through them. The liquid hydrogen sulfide was transferred directly from the generator to these after they had been cooled in a freezing mixture of ether and solid carbon dioxide contained in Dewar bulbs.

The reactions were allowed to take place at that temperature (about −77°) and at the same time other tubes were sealed at this temperature and then permitted to come to room temperature at which they were kept for a week or more, if necessary. for any slow reaction to take place. After the reaction had taken place at either temperature the excess of liquid hydrogen sulfide and any volatile substances were permitted to evaporate

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[1] This paper is from a portion of the work presented by A. W. Ralston in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Iowa State College.

[2] Quam, THIS JOURNAL, 47, 103 (1925).

[3] Quam and Wilkinson, *ibid.*, 47, 989 (1925).

and the residue was examined by analysis to find whether any reaction had taken place and if so what products had been formed.

The samples for analysis were weighed in small glass capsules which were broken beneath the surface of a concentrated solution of potassium hydroxide contained in a stoppered vessel. This prevented any loss of hydrogen sulfide. This solution was used for analyses.

Data

The chlorides of the alkali metals and of the alkali earth metals, $CuCl_2$, $CdCl_2$, $MnCl_2$, $CoCl_2$, $FeCl_2$ and $CrCl_3$ (both the green and violet forms) are insoluble and non-reactive in liquid hydrogen sulfide both at low temperature and at room temperature. Cuprous chloride and silver chloride react with liquid hydrogen sulfide, the former blackening immediately and the latter reacting more slowly to form a flocculent, yellow solid which turns black on exposure to the air. Hydrogen chloride is liberated, showing that some thiohydrolysis has taken place.

Zinc chloride is slightly soluble at the low temperature and more soluble at room temperature, although it is non-reactive at all temperatures. The halides of mercury where the valence is two are soluble but non-reactive at the low temperature, the iodide being the most soluble and the chloride the least. The solubility increases with rise of temperature and at room temperature the chloride is thiohydrolyzed to the black sulfide, which later turns to the red form. The iodide is not thiohydrolyzed but on the evaporation of the liquid hydrogen sulfide the iodide crystallizes out as the yellow form which later turns to the stable red form.

Mercurous chloride is insoluble in liquid hydrogen sulfide but reacts even at the low temperature to form a brown, flocculent, gelatinous mass which on analysis was found to contain 85.81% of Hg and 13.65% of S, which is very close to the composition of HgSH (85.85% of Hg and 13.72% of S). It cannot be mercurous sulfide (92.6% of Hg and 7.4% of S) and it is unlikely that it is a mixture of mercuric sulfide and mercury, not only from the brown color but also because hydrogen sulfide is shown to be a strong reducing agent with other elements such as titanium, selenium and tellurium and so it would hardly be expected to permit the oxidation of the HgSH to mercuric sulfide.

Boron trichloride and aluminum chloride are both quite soluble in liquid hydrogen sulfide. The former reacts very vigorously, even at the temperature of the ether and solid carbon dioxide mixture, forming a white, crystalline compound. As the temperature is raised, this compound melts to a clear liquid at $-47°$ from which the crystals again separate on cooling. Due to its low melting point and to its instability it was impossible to get a weighed sample for analysis to find the per cent. and the formula. However, by adding an unweighed quantity of the crystals to a solution of potassium hydroxide and analyzing aliquot portions of this for the weights of boron, chlorine and sulfur, the formula of the solid may be calculated. The chlorine was determined by the Volhard titration with silver nitrate and ammonium thiocyanate and the sulfur by distilling, after acidifying with hydrochloric acid, into ammoniacal cadmium chloride and titrating with standard iodine solution. The boron was determined by distilling it as methyl borate, saponifying with lime and weighing as boron trioxide. Two hundred cc. of such a solution showed 0.0344 g. of boron trioxide and other 200cc. portions required 48.4 and 48.32 cc. of silver nitrate solution, one cc. of which is equivalent to 0.00217 g. of chlorine. Twenty-five-cc. portions were used to determine the sulfur and they required 29.57 cc. and 29.68 cc. of an iodine solution, one cc. of which is equivalent to 0.001585 g. of sulfur. This shows that there was present in the unweighed sample 0.0344 g. of boron trioxide or 0.01069 g. of boron, 0.10503 and 0.10485 g. of chlorine and 0.37495 and 0.37632 g. of sulfur. Calculating the formula from these results shows quite clearly that the formula for the compound is $BCl_3.12H_2O$.

This calculation is made by dividing the weight of each element by its respective atomic weight and finding the ratios of these quotients which will give the relative number of atoms that are present in the compound.

Aluminum chloride shows solubility but no thiohydrolysis, and no thiohydrates were found to crystallize out on evaporation although Biltz[4] has shown the existence of thiohydrates of aluminum choride by vapor pressure measurements. Quam reported aluminum choride as insoluble and non-reactive but there is definite evidence of the fact that it dissolves as shown in the conductance of the solution, which will be discussed later.

In the fourth group of the periodic table where the elements become more non-metallic the solubility of the chlorides in liquid hydrogen sulfide becomes quite marked. Carbon tetrachloride and silicon tetrachloride are miscible with liquid hydrogen sulfide in all proportions and show practically no thiohydrolysis. However, when silicon tetrachloride was kept at room temperature with hydrogen sulfide for several weeks a small amount of brown silicon disulfide was formed. Stannic chloride, which freezes at $-33°$ is insoluble and non-reactive at the low temperatures but at room temperature the two liquids are miscible. After standing for two weeks at this temperature a small amount of yellow stannic sulfide was formed. Biltz[4] has shown that plumbic chloride is reduced to plumbous chloride. This group of chlorides which are so easily hydrolyzed in water are very inert in liquid hydrogen sulfide. It should, therefore, be an excellent medium in which to study the reactions of these compounds.

Titanium tetrachloride at very low temperatures forms a yellow crystalline body, the composition of which is shown by analysis to be $2TiCl_4.H_2S$.

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[4] Biltz, *Z. anorg. allgem. Chem.*, **147, 171 (1925).**

This compound is very unstable and decomposes into titanium tetrachloride and hydrogen sulfide as the temperature is slowly raised. If it is rapidly warmed to room temperature the decomposition takes place almost explosively. It is therefore impossible to get a weighed portion of this addition product, due to its instability. By allowing the excess of hydrogen sulfide to evaporate off at $-77°$ and taking an unweighed portion of the residue and dissolving in potassium hydroxide solution, as was done with the boron compound, the formula may be determined. The following values were obtained.

Titanium. 0.0378 g. of $TiO_2 = 0.0378/80.1 = 0.000472$ atom $= 2 \times 0.000233$.
Chlorine. 0.2674 g. of $AgCl = 0.2674/143.3 = 0.001866$ atom $= 8 \times 0.000233$.
Sulfur. 0.0544 g. of $BaSO_4 = 0.0544/233.4 = 0.000233$ atom $\approx 1 \times 0.000233$.

This shows that the formula for the compound is $2TiCl_4.H_2S$.

Biltz[4] reported only two thiohydrates of $TiCl_4$, $TiCl_4.2H_2S$ and $TiCl_4.H_2S$.

At room temperature the reaction between liquid hydrogen sulfide and titanium tetrachloride is very vigorous. A brown solid is first formed which is soluble in the liquid hydrogen sulfide giving a red solution. Later a layer of black solid mixed with a yellow one forms. When this mass is extracted for a long time with carbon disulfide, the yellow dissolves and is found to be sulfur, showing that some reduction has taken place. The black residue was analyzed and found to be titanous chloride. The brown solid which is first formed is soluble in alcohol, giving a solution with a decided mercaptan odor. Pfordten[5] prepared similar compounds by the action of dry hydrogen sulfide gas on titanium tetrachloride. Titanium tetrachloride seems to be one of few chlorides studied where it is possible that the thiohydrolysis first gives an SH body corresponding to the OH in hydrolysis. Further work is being done on the reaction between hydrogen sulfide and titanium tetrachloride.

Phosphorus trichloride is partly miscible but non-reactive at low temperatures with liquid hydrogen sulfide but P_2S_3 is formed immediately on mixing at room temperature. Phosphorus pentachloride immediately forms the insoluble $PSCl_3$ at all temperatures. This resembles the similar reaction with water except that there the hydrolysis is completed forming the soluble hydroxide or acid.

Arsenic trichloride gives the sulfide, As_2S_3, immediately at all temperatures. This also differs from the similar reaction in water where the soluble hydroxide or acid is formed. Antimony trichloride shows that the element is more metallic than arsenic in that it does not dissolve or react with the hydrogen sulfide at low temperature as does arsenic trichloride. It is very soluble but non-reactive at room temperature. In either case, however, when the liquid hydrogen sulfide is evaporated off, the antimony

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[5] Pfordten, *Ann.*, 234, 257 (1886).

trichloride reacts with the vapor of hydrogen sulfide to form lemon-yellow crystals and hydrogen chloride is evolved. These crystals were analyzed and found to be $SbSCl.7SbCl_3$. The data obtained are as follows.

Anal. **Calcd.: Sb, 54.21; Cl, 43.98; S, 1.81. Found: Sb, 54.12; Cl, 43.86; Cl, 1.87.**

This same compound has been prepared by Schneider[6] by the action of dry hydrogen sulfide gas on dry antimony trichloride at reduced temperatures.

Antimony pentachloride reacts similarly to phosphorus in hydrogen sulfide forming the $SbSCl_3$. It is more thiohydrolyzed in hydrogen sulfide than it is hydrolyzed in water since the antimony chloride is hydrolyzed only in warm water. Bismuth trichloride reacts immediately, even at low temperatures, with liquid hydrogen sulfide forming an orange-red solid. This solid slowly gave off hydrogen chloride but after standing in a desiccator over sulfuric acid for several days it arrived at constant weight and an analysis showed it to be Bi_2SCl_4 or $BiSCl.BiCl_3$.

Anal. **Calcd. for Bi_2SCl_4: Bi, 70.62; Cl, 23.96; S, 5.42. Found: Bi, 70.49; Cl, 23.91; Cl, 5.52.**

It seems therefore that an addition product or thiohydrate is first formed which slowly loses hydrogen chloride in the air, forming the basic salt. This corresponds to the action of hydrogen sulfide on titanium tetrachloride except that in the case of bismuth trichloride the addition product is more stable. The formation of the insoluble addition product accounts for the fact that Quam and Wilkinson[3] found that a mixture of bismuth trichloride and hydrogen sulfide did not conduct an electric current in spite of the fact that a visible reaction had taken place. The same body is formed with bismuth trichloride at room temperature.

Selenium tetrachloride at low temperatures reacts slowly with liquid hydrogen sulfide until all of it has disappeared. After boiling off the excess of hydrogen sulfide, a yellow solid remains. When the temperature is raised, this solid melts to a red-brown liquid which has sulfur suspended in it. An analysis of this liquid showed it to be Se_2Cl_2. At room temperature selenium tetrachloride reacts rapidly with hydrogen sulfide and is reduced to red selenium. This can be separated from the sulfur mixed with it by means of the greater solubility of the selenium in carbon disulfide compared to the sulfur.

Tellurium tetrachloride in the cold is reduced immediately to tellurium dichloride and sulfur, the former being insoluble in carbon disulfide while the latter dissolves slowly. At room temperature the tellurium tetrachloride, like selenium tetrachloride, is completely reduced to the element.

Chromium trichloride, either the green or violet form, is insoluble and does not react with hydrogen sulfide at any temperature. This is a little

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[6] Schneider, *Pogg. Ann. phys. Chem.*, **108,407 (1859).**

unusual considering that the trivalent chlorides, aluminum chloride and ferric chloride, are both soluble. Manganous chloride and cobalt chloride are insoluble and non-reactive at low temperature although cobalt chloride will turn black on long standing at room temperature.

Ferric chloride dissolves to a yellow liquid from which, at low temperatures, a white precipitate of ferrous chloride slowly separates. At room temperature the same reaction takes place very rapidly.

Conductance of Chloride Solutions in Liquid Hydrogen Sulfide

In order to check the conclusions as to whether or not the chlorides dissolved in the liquid hydrogen sulfide, the conductances of the solutions were determined after they had stood until equilibrium had been reached. The cells used were similar to those described by Quarn and Wilkinson[3] and the conductance was measured at the temperature of the mixture of ether and solid carbon dioxide.

Potassium, strontium, barium, cadmium, chromic (green and violet forms), manganous and cobalt chlorides all showed non-conductance.[7] Silver, cuprous and mercurous chlorides all show some conductance after standing, due to the hydrogen chloride liberated by the thiohydrolysis. The specific conductances for solutions of the other chlorides are given in the following table.

TABLE I

CONDUCTANCES OF SATURATED SOLUTIONS OF CHLORIDES IN LIQUID HYDROGEN SULFIDE

Pure H_2S, λ = (1×10^{-11})		Pure H_2S, λ = (1×10^{-11})	
Salt	$\lambda \times 10^6$	Salt	$\lambda \times 10^6$
$HgCl_2$	0.031	$AlCl_3$	2.092
$SnCl_4$	.106	$HgBr_2$	5.16
$SiCl_4$	.129	HgI_2	9.99
$ZnCl_2$	.634	$FeCl_3$	209.9
HCl	.881	$SbCl_3$	424
$AsCl_3$	1.15		

Conclusions

A study of the chlorides in different parts of the periodic table shows that the chlorides of the metallic elements are mostly insoluble in liquid hydrogen sulfide except zinc, mercuric, aluminum and ferric chlorides. The univalent chlorides of silver, copper and mercury are insoluble but thiohydrolyze to insoluble hydrosulfides or sulfides.

The chlorides of the non-metallic elements which are easily hydrolyzed in water forming the hydroxides are, in many cases, soluble in liquid hydrogen sulfide in all proportions and show no thiohydrolysis. In other cases they form thiohydrates, addition products and sulfides but there

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[7] In the paper by Quam and Wilkinson (ref. 3) the statement is made that the specific conductance of pure liquid hydrogen sulfide is half that of water. This is obviously an error as the figures which are given show that it is one hundred thousandth as much.

is little evidence that any of them form a thio-acid such as H_3AsS_3, except possibly $TiCl_4$.

The reducing action of hydrogen sulfide accounts for many of the differences encountered in comparing these reactions with similar ones in water, for example, with $TeCl_4$, $SeCl_4$, $TiCl_4$ and $FeCl_3$.

AMES, IOWA

[FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, BEDFORD COLLEGE, UNIVERSITY OF LONDON]

THE POSITION OF THE ELEMENTS OF THE RARE EARTHS IN THE PERIODIC SYSTEM

BY J. F. SPENCER

RECEIVED MAY 2, 1927 PUBLISHED FEBRUARY 4, 1928

From the time when Mendeléeff enunciated the principles of the periodic system, many attempts have been made to include the elements of the rare earths in the classification. Previous to 1870 the rare earth elements were regarded as divalent, chiefly because of the strongly basic character of their oxides. Mendeléeff, finding difficulty in placing the then known elements of the rare earths in Group II of his system, contended that the metals are tervalent. He, therefore, assigned to yttrium, didymium and erbium positions in Group III and to cerium and lanthanum positions in Group IV. The work done on the rare earths since 1870 has confirmed Mendeléeff's view of the tervalency of these elements and at the same time it has increased their number from five to seventeen. There are included in this remarkable series of elements, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, illinium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium. The order given above is that of ascending atomic number.

The element illinium (atomic number 61) has recently been recognized by Lapp, Rogers and Hopkins[1] by means of x-ray analysis of rare earth fractions, and thus a complete series of elements of atomic numbers 57 to 71 is made up. In order of atomic number lanthanum (57) follows barium (56) and hafnium (72) follows lutecium (71). Consequently it may be taken that the series of rare earths is complete.

Since the time of Mendeléeff many attempts have been made to arrange these elements either in Mendeléeff's system, in modifications of Mendeléeff's system or in geometrical systems by Brauner, R. J. Meyer, Retgers, Benedicks, Soddy, Stefan Meyer, Steele, Werner, Vogel, Rydberg, Aston, Bohr and others. The arrangements in Mendeléeff's system have failed because of an apparent lack of accommodation and because valencies have been assigned to certain of the elements which could not be sub-

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[1] Lapp, Rogers and Hopkins, *Phys. Rev.*, 25, 106 (1925).

stantiated. The arrangements in modified forms of the Mendeléeff system have destroyed the symmetry, simplicity and usefulness of the periodic classification, and the arrangement in geometrical systems, whilst often useful, is not necessarily an arrangement in the periodic system.

What follows is an attempt to place these elements in the Mendeléeff system in its original form. Hence, without considering any of the previous attempts in detail, the present attempt may be put forward.

From a consideration of the whole of the elements from the point of view of the ease with which they may be separated from one another it becomes evident that they may be sub-divided into four groups thus: (I) elements which are readily separable from each other, that is, elements like sodium, silver, oxygen, chlorine, etc., (II) elements which are difficult to separate from each other; this group comprises the triads of Group VIII of Mendeléeff's system: iron, cobalt, nickel; ruthenium, rhodium, palladium; osmium, iridium, platinum; (III) elements which are very difficult to separate, this group includes the rare earths; and (IV) elements which, for practical purposes, are inseparable, the isotopes. Each of the elements of the first group occupies alone a place in the Mendeléeff system; the elements of the second group are placed three in a single place of the system and the elements of the fourth group, the isotopes, are placed many in a single space; thus there are at least eleven isotopes of lead, five of bismuth, four of zinc, seven of xenon and six of thorium. The isotopes of a given element have the same atomic number and properties and they are therefore all placed in the same place of the periodic system. Furthermore, this in no way destroys the Mendeléeff system nor impairs its symmetry and usefulness to the chemist.

The tervalency of the elements of the rare earths has been established beyond all doubt from (I) the specific heat of the metals, (II) the molecular weight of the anhydrous chlorides in absolute alcohol solution, (III) the molecular weight of the acetyl acetonates in carbon disulfide solution, (IV) the isomorphism of the octahydrates of the sulfates and (V) the equivalent conductance of aqueous solutions of the chlorides and sulfates. Consequently all of the seventeen elements yield an oxide M_2O_3 and a chloride MCl_3.

In addition, cerium, neodymium, praseodymium and terbium yield a dioxide MO_2, whilst europium and samarium yield a dichloride MCl_2. The two elements of smallest atomic number, scandium and yttrium, find places in the periodic system without difficulty; they fall naturally following the order of atomic numbers into Group III, Series 4 and 6, respectively. This leaves fifteen elements which form *a* complete series, lanthanum (57)—lutecium (71), to be placed between barium *(56)* and hafnium (72). Since these elements are basic, show no marked acidic properties and are all tervalent, they must all be accommodated in the six places of the periodic system, in Groups III and IV, Series 8, 9 and 10. Here it is that the difficulty of the problem becomes apparent; any one of these elements with the exception of cerium might from its chemical properties go into Group III, Series 8, and cerium would naturally go into Group IV, Series 8.

It has been shown by Weiss,[2] from measurements of the ionic magnetic moment, made by Cabrera and Stefan Meyer with the octahydrates of the sulfates of these elements, that when the ionic magnetic moments are plotted as abscissas against the number of electrons in the cations, a double curve is obtained (Fig. 1) which divides these elements into two groups, (I) lanthanum, cerium, neodymium, praseodymium and samarium, (II) europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium.

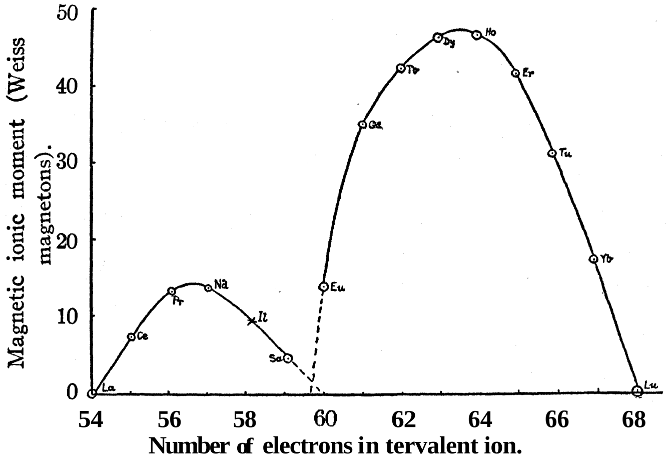

Fig. 1.

The element illinium (61) must be taken to come between neodymium and samarium. These two groups are practically identical with the two groups which may be made from the order of the solubility of the sulfates of the rare earths in saturated solutions of alkali sulfates; (I) practically insoluble, lanthanum, cerium, praseodymium, neodymium and samarium; (II) europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium; the first three members of the second group are sparingly soluble and the remainder are more soluble than in water. The first three elements of the second group, that is, the terbium earths, fall on the ascending branch of the second half of Weiss' curve and the others on the descending branch.

From the above facts and the general chemical characteristics of the

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[2] *Journ. de Phys.*, 1925, Bull., 218, 86 S.

rare earth elements it appears that they may be placed in the periodic system as shown below.

TABLE I

	II		III		IV		V	
	A	B	A	B	A	B	A	B
4	Ca		Sc		Ti		V	
5		Zn		Ga		Ge		As
6	Sr		Yt		Zr		Nb	
7		Cd		In		Sn		Sb
8	Ba		La		Ce, Pr, Nd, Il		. . .	
9	. . .			Sa, Eu, Gd		Tb	. . .	
10	. . .		Dy, Ho, Er, Tu, Yb, Lu		Hf		Ta	

Leaving samarium out of account for the moment, the elements on the first half of Weiss' curve (the cerium earths) fall into Series 8; those on the rising branch of the second half of the curve (the terbium earths) fall into Series 9 and those on the falling branch of the second half of the curve fall into Series 10 (yttrium earths). Samarium sulfate may be equally well regarded as the most soluble of the insoluble cerium earth sulfates in saturated alkali sulfate solutions or as the least soluble of the sparingly soluble sulfates. That is, the solubility series given above may be written (I) insoluble: lanthanum, cerium, neodymium, praseodymium; (II) sparingly soluble: samarium, europium, gadolinium, terbium; (III) soluble: dysprosium, holmium, erbium, thulium, ytterbium, lutecium. The solubility sub-division is now the same as that in the periodic system.

Lanthanum is put in Group 111 A, Series 8, because its oxide is the strongest base of the rare earths and naturally follows barium; cerium, praseodymium and neodymium are placed in order of atomic number in Group IV A, Series 8, since they all form dioxides and sesquioxides, as also do titanium and zirconium, which precede them in Group IV A. The new element illinium must also be placed there because its ionic magnetic moment will undoubtedly fall between the moments of neodymium and samarium on the Weiss curve; samarium, europium and gadolinium are placed in Group III B, Series 9; of these europium and samarium form dichlorides, a type of compound also formed by the other members of Group III B, gallium, indium and thallium. A dichloride is unknown in the case of gadolinium but in the present state of our knowledge of gadolinium compounds this is no reason for stating that such a compound cannot exist; further, gadolinium is very like europium and samarium in its general behavior, so much so that gadolinium and samarium were separated together from Mosander's didymium by Delafontaine,[3] and for a time regarded as a single element, decipium. The

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[3] Delafontaine, *Compt. rend.*, **87, 559, 634 (1878).**

six elements dysprosium, holmium, erbium, thulium, ytterbium and lutecium come in order of atomic number into Group III A, Series 10. These metals are typically tervalent and each of them could be placed in this position. If the reasons given above be accepted, these six elements must all go into this position. Between lutecium (71) and tantalum (73) in Series 10, there is still a vacant place in group IV A into which hafnium (72) naturally goes. The scheme presented places the whole of the elements of the rare earth group into Mendeléeff's periodic system without destroying its symmetry or impairing its utility in the slightest. It is difficult to submit the scheme to a rigorous test because many essential data are lacking; but a broad line taken through the existing chemical and physical data confirms, in general, the present arrangement.

London, England

[Contribution from the Chemical Laboratory of Princeton University]

SIMPLE BIMETALLIC ELECTRODE SYSTEMS FOR POTENTIOMETRIC TITRATIONS. I. THE APPLICATION OF THE PLATINUM-GOLD AMALGAM SYSTEM TO CERTAIN OXIDATION-REDUCTION TITRATIONS

By N. Howell Furman

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Introduction

Hostetter and Roberts[1] suggested the possibility of substituting a palladium wire for the calomel half-cell that is generally used as a reference electrode in potentiometric titrations. Willard and Fenwick[2] have studied a large number of possible systems that consist of two dissimilar metallic electrodes. They did not, however, study amalgamated electrodes.

This investigation grew out of a study of certain platinum electrodes that were unintentionally "poisoned" with mercury. These electrodes behaved temporarily like mercury electrodes. It has not thus far been found possible to prepare amalgamated platinum electrodes that serve over long periods of time as mercury electrodes.

Amalgamated gold electrodes were found to behave like calomel electrodes in solutions that contained chloride and like mercurous sulfate electrodes in solutions that contained sulfate. During the course of most oxidation-reduction titrations the concentration of chloride or sulfate varies. Nevertheless, an amalgamated gold electrode will serve as a satisfactory reference electrode for such titrations. The reducing action of the minute quantity of mercury or gold that is in contact with

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[1] Hostetter and Roberts, This Journal, 41, 1343 (1919).

[2] Willard and Fenwick, *ibid.*, 44, 2504 (1922).

the solution does not occasion any systematic error when the reagents are as dilute as 0.05 N.

Experimental

Electrodes.—The gold amalgam electrodes were of the construction indicated in Fig. 1. The Bakelite block, e (6 × 3 × 0.5 cm. drilled with 6 holes of 0.45 cm. diameter), was found to be a very convenient support that permitted ready interchange of electrodes. Gold of C. P. grade from two sources (foil 0.23 mm. thick from the United States Mint and wire of 0.33 mm. diameter (28 gage B. and S.) from Baker and Co., Inc., Newark, N. J.) was used. A momentary immersion of the exposed gold tip in pure mercury effected the amalgamation. It was not found advisable to put a drop of mercury within the tube because of leakage of mercury through the gold. Molten paraffin was poured into the glass tubes (see Fig. 1) as a safeguard against leakage. (A number of electrodes served satisfactorily for long periods without the paraffin seal.) The amalgamated tip is immersed in dilute hydrochloric acid when the electrode is not in use. Electrodes that dry in air become sluggish. They may be reactivated by wiping the amalgamated tip and dipping it anew in mercury.

It was found by heating portions of the tips of a number of electrodes that the initial percentage of mercury was between 15 and 20. It was anticipated that the reducing action of the mercury might be objectionable. McCay and Anderson[3] have shown that ferric iron, chromic acid, vanadic acid and other oxidizing agents are reduced quantitatively to lower states of oxidation when shaken with a large excess of mercury in the presence of a suitable amount of chloride. The tips of the electrodes that dipped into the solutions contained at most 2 mg. of mercury—a quantity capable of reducing only 10^{-5} g. equivalent, or 0.01 cc. of N solution. Only a small part of the 2 mg. or less of mercury is actually in contact with the solution. After a large number of titrations mercury is still visible in the electrodes.

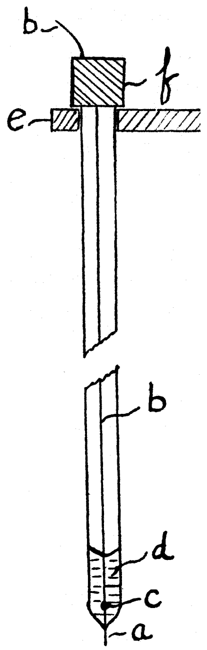

Fig. 1.—Amalgamated gold electrode. (a) Amalgamated tip of a gold wire that is sealed through the glass. Soft glass was used and care was taken not to fuse the gold. (b) Copper wire fused to gold at point (c). The upper end of (b) is wrapped around the glass tube and is held in position by rubber tubing (f). The shaded portion (d) represents paraffin.

There was a relatively large unintentional variation in the total time of titration. In a few instances that were noted as long as twenty minutes elapsed between the time that the solution was first stirred in contact with the electrodes and the start of the titration with ferrous sulfate. In a number of other instances interruptions occurred after a titration had proceeded a short distance. It was not necessary to reject any determinations that were interrupted nor was any definite trend due to this cause noted.

Thus far no tests have been made of the effectiveness of the Pt-Hg(Au) system with reagents more dilute than 0.05 N.

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[3] McCay and Anderson, THIS JOURNAL, 43, 2372 (1921); 44, 1018 (1922).

Apparatus.—A Leeds and Northrup Co. students' type potentiometer and a portable galvanometer (type 2320 d) of 0.5 micro-ampere sensitivity were used.[4] All volumetric apparatus had been carefully calibrated.

Procedure.—Tenth or 0.05 N solutions of oxidizing and reducing agents were standardized potentiometrically. Anhydrous sodium oxalate of known purity was the primary standard. Bichromate and permanganate solutions were compared by as nearly as possible simultaneous potentiometric titrations of portions of a solution of Mohr's salt.

Titrations with the usual system[5] were interspersed with those made with the Pt-Hg(Au) combination. No attempt was made to free the solutions from dissolved air by working in an inert atmosphere. This may affect the accuracy of the results with the 0.05 N solutions but should not affect the precision of the comparison of the two electrode systems because both sets of titrations were made under as nearly as possible identical conditions.

The Bichromate-Ferrous Iron Reaction.—The average of at least three concordant determinations by the usual potentiometric method was assumed to be correct. The volume was 100 cc. at the start of each titration. The general conditions that were employed will be evident from Table I.

TABLE I

TITRATION OF APPROXIMATELY 0.1 *N* POTASSIUM BICHROMATE WITH FERROUS SULFATE

		1	2	3	4	5	6
I. Cc. of $FeSO_4$ (Pt-N. C. E.)		10.00	10.00	25.01	25.01	25.01	25.01
II. Cc. of $FeSO_4$ (Pt-Hg(Au))		10.04	10.04	24.98	25.00	24.98	24.96
Difference (II–I)		+0.04	+0.04	−0.03	−0.01	−0.03	−0.05
Acid present, cc.	12 *N* HCl	15	15	15	15	...	...
	6 *N* H_2SO_4	...	...	...	...	25	25

The reverse titration was then studied, varying the experimental conditions in a similar manner. The differences in quantities of bichromate that were found by using the two systems were: +0.07, +0.02, +0.03, −0.04, +0.02, −0.03, −0.05 and +0.02 cc. of 0.1 N potassium bichromate.

Further comparisons of the two systems were made with 0.05 *N* solutions; differences found: cc. of 0.05 *N* $FeSO_4$: +0.01, +0.02, —0.03, —0.02, +0.01 and —0.05; and in the reverse titration the differences were cc. of 0.05 N $K_2Cr_2O_7$: —0.07, —0.04, +0.02, —0.06, —0.02, +0.04 and +0.01.

The values in Table I, and the paragraphs that follow it, have been

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[4] For further details of the apparatus, see Furman, J. Chem. Education, 3, 936 (1926).

[5] Hereafter designated as Pt-N. C. E. When necessary a salt bridge of N potassium sulfate solution was interposed between the normal calomel electrode and the titration beaker.

calculated to cc. of exactly 0.1 or 0.05 N solution. The actual normalities of the bichromate solutions were 0.1000 and 0.05098. The substitution of the amalgamated gold electrode for the N calomel electrode does not cause any systematic error. The average deviation of the values from the mean is practically the same with both systems.

Graphs that are constructed from the titration data show some interesting features. When the solutions contain chloride, the curves (Pt-Hg(Au) system) are very similar to those that are obtained with the Pt-N.C.E. system. They are merely displaced upward on the e.m.f. axis (see Fig. 2) because the chloride concentration is usually greater than N.

In solutions that contain sulfuric acid and sulfates, the curves resemble closely those obtained with Pt-N potassium sulfate-N mercurous sulfate system. When the surface of the electrode becomes depleted of mercury by long use, the curves representing the titration of bichromate with ferrous sulfate show a pronounced sweep upward before the end-point. This is characteristic of the Pt-Au system.[6]

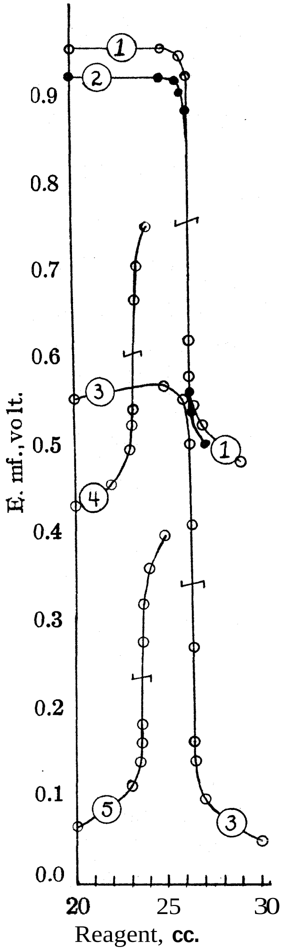

Fig. 2.—Typical plots of titration data. Curves 1, 2 and 3 represent the titration of 25 cc. portions of 0.1000 *N* $K_2Cr_2O_7$ with an approximately 0.1 *N* ferrous sulfate solution, first with Pt-Hg(Au) system, second with Pt-N. C. E., both in HCl solution, and the third with the Pt-Hg(Au) system in H_2SO_4 solution. Curve (4) represents titration of 25 cc. of approximately 0.05 *N* $FeSO_4$ in HCl solution and (5) titration of 25 cc. of approximately 0.1 N $FeSO_4$ in H_2SO_4 solution with the Pt-Hg (Au) system. Bichromate was the oxidant in both cases.

The Permanganate-Ferrous Iron Reaction.—The permanganate solutions were 0.0518 and 0.0510 N, respectively. The values found have been calculated to cc. of exactly 0.05 N solutions. A salt bridge of N potassium sulfate solution was interposed between the N calomel cell and the titration beaker.

In the titration of ferrous sulfate with permanganate the differences, expressed in cc. of 0.05 *N* potassium permanganate, were: +0.01, −0.03, −0.06, −0.05, −0.03 and ±0.00.

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[6] A detailed study of the Pt-Au system is presented in the second paper of this series, THIS JOURNAL, 50, 273 (1928).

The data for the reverse titration are presented in Table II.

TABLE II

TITRATION OF APPROXIMATELY 0.05 N PERMANGANATE WITH FERROUS SULFATE

	1	2	3	4	5
I. Cc. of $FeSO_4$ (Pt-N. C. E.)	25.50	25.50	25.50	10.20	10.20
II. Cc. of $FeSO_4$ (Pt-Hg(Au))	25.51	25.51	25.44	10.18	10.21
Difference (II − I)	+0.01	+0.01	−0.06	−0.02	\$0.01

In each instance the initial volume was 50 cc., containing 25 cc. of 6 *N* H_2SO_4.

The potentiometric titration of permanganate with ferrous sulfate must be carried out under the conditions that were established by Miiller and Möllering.[7] They found that the acid concentration must be sufficiently high and that the ferrous sulfate must be added rapidly until the end-point is closely approached. The permanganate color disappears a few drops before the end-point is reached. The work of Miiller and Möllering explains this fact in terms of the reactions

$$Mn^{VII} + 3Fe^{II} = Mn^{IV} + 3Fe^{III}, \text{ and} \qquad (1)$$
$$Mn^{IV} + 2Fe^{II} = Mn^{II} + 2Fe^{III} \qquad (2)$$

that occur simultaneously. The author's experience is entirely in accord with these views. It was found, for example, that slow addition of ferrous sulfate to 25 cc. of 0.05 N permanganate in a volume of 100 cc. containing 25 cc. of 6 *N* sulfuric acid caused a very considerable separation of manganese dioxide (Equation 1). All determinations in which there was any visible precipitation of manganese dioxide were inaccurate.

The **Vanadic** Acid-Ferrous Sulfate Reaction.—The normality of the vanadic acid solution was established by titration with ferrous sulfate that had been titrated potentiometrically with standard permanganate solution. Found: vanadic acid 0.05596 N (average) by the potentiometric method, and 0.05597 N (average) when diphenylamine was used as indicator.[8,9]

TABLE III

TITRATION OF 0.05597 *N* VANADIC ACID WITH 0.0488 *N* FERROUS SULFATE

	1	2	3	4	5
Cc. of vanadic acid	25	25	25	25	10
$FeSO_4$ calcd., cc.	28.67	28.67	28.67	28.67	11.46
$FeSO_4$ found, cc.	28.62	28.68	28.70	28.66	11.50
Error, cc.	−0.05	+0.01	+0.03	−0.01	+0.04

In nos. 1–2, 15 cc. of concd. HCl (sp. gr. 1.2), and in nos. 3–5, 25 cc. of 6 N sulfuric acid were present. The initial volume was 50 cc. in each determination.

The graphs of the titration data present no unusual features.

[7] Miiller and Mollering, Z. *anorg. allgem.* Chem., 141, 111 (1924).

[8] Someya, *ibid.*, 139, 237 (1924); 152,391 (1926).

[9] Furman, *Science*, 59, 560 (1924); *Ind. Eng. Chem.*, 17, 314 (1925).

Discussion

A number of incidental observations have been made upon the use of the amalgamated gold electrode in other oxidation-reduction reactions. The results were satisfactory in all instances. Six different electrodes, three of foil and three of gold wire, were used in the progress of the work. All served satisfactorily. The especial advantages of these electrodes are their simplicity and the fact- that in solutions that contain chloride the voltage readings are very close to those that are obtained with the familiar Pt-N. C. E. system.

Preliminary observations have shown that the amalgamated gold electrode may be used in following neutralizations of hydrochloric or sulfuric acid; also that such electrodes serve as indicator electrodes for certain precipitation reactions, for instance, precipitation of halides with silver, or vice versa, It is planned to make a detailed study of some of these possible applications of gold amalgam as an indicator electrode.

Summary

A small amalgamated gold electrode has been shown to be a suitable reference electrode for several kinds of potentiometric oxidation-reduction titrations with reagents as dilute as 0.05 N.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

SIMPLE BIMETALLIC ELECTRODE SYSTEMS FOR POTENTIOMETRIC TITRATIONS. II. NOTES ON THE USE OF THE PLATINUM-GOLD ELECTRODE SYSTEM

BY N. HOWELL FURMAN

RECEIVED JUNE 17, 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

A knowledge of the platinum-gold system was found to be desirable in connection with a study of the platinum-gold amalgam electrode system that has been described in the former communication.[1] The construction of electrodes, electrical apparatus, and mode of procedure were there described.

Experimental

Titration of Permanganate with Ferrous Sulfate.—The general form of the graph of the titration data is indicated in Fig. 1. There is always a sharp rise to a "peak" in e.m.f. just before the end-point. The position of this peak is extremely variable (see Table I). The drop in voltage at the end-point is unmistakable.

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[1] Furman, THIS JOURNAL, 50, 268 (1928).

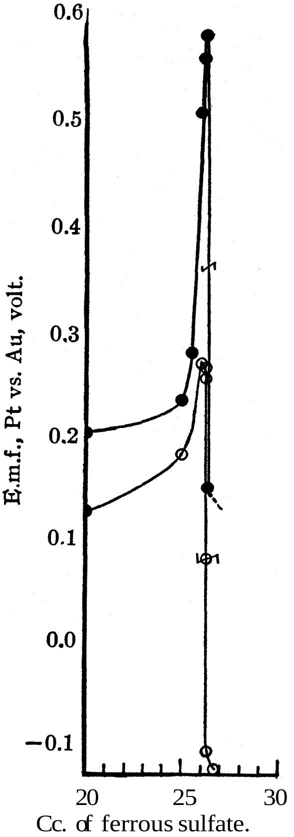

Fig. 1,— Characteristic curves, permanganate-ferrous sulfate reaction, followed by Pt-Au system, showing variability of peak of e.m.f.

TABLE I

TITRATION OF APPROXIMATELY 0.05 *N* PERMANGANATE WITH FERROUS SULFATE

No.	FeSO$_4$ calcd., cc.	FeSO$_4$ found. cc.	Error, cc.	Difference in voltage, Pt vs. Au		
				(a) Initial	(b) Maximum	(c) Break at end-point (1 or 2 drops)
1	26.32	26.30	−0.02	0.180	0.671	0.496 (1 drop) FeSO$_4$
2	26.32	26.28	− .04	.153	.622	.482 FeSO$_4$
3	26.32	26.26	− .06	.175	.330	.454 FeSO$_4$
4	26.32	26.33	+ .01	.150	.279	386 { 0.186 1st drop .200 2nd drop
5	10.52	10.46	− .06	.169	.424	.482 { .305 1st drop .177 2nd drop
6	10.52	10.58	+ .06	.177	.392	.486 1 drop
7	10.52	10.53	+ .01	.186	.340	.455 1 drop

The initial volume was 50 cc. in each case, with 25 cc. of 6 N sulfuric acid present.

The precautions noted by Miiller and Möllering[2] were carefully followed in order to avoid formation of any appreciable amount of manganese dioxide.

The Bichromate–Ferrous Iron Reaction.—The ferrous sulfate solutions were frequently restandardized by potentiometric titration with potassium bichromate. The results of the titrations using the Pt-Au electrode system are presented in Tables II–IV.

TABLE II

TITRATION OF APPROXIMATELY 0.05 *N* BICHROMATE WITH FERROUS SULFATE

No.	Calcd., cc.	Ferrous sulfate Found, cc.	Error, cc.	E.m.f. difference, Pt vs. Au (a) Initial	(b) Maximum	(c) Break per 1 drop of $FeSO_4$
1	26.16	26.11	−0.05	0.144	0.176	0.187
2	26.16	26.11	− .05	.246	.315	.200
3	26.16	26.13	− .03	.241	.332	.211
4	26.16	26.19	+ .03	.218	.427	.270
5	26.16	26.17	+ .01	.207	.368	.122

In determinations 1, 4 and 5, 5 cc. of concd. sulfuric acid (sp. gr. 1.84) and in nos. 2 and 3, 10 cc. of hydrochloric acid of sp. gr. 1.2 were present. The initial volume was 50 cc.

The determinations in Tables III and IV were made by Mr. H. H. Carspecken, to whom the author wishes to express his indebtedness.

TABLE III

TITRATION OF APPROXIMATELY 0.1 *N* FERROUS SULFATE WITH BICHROMATE

No.	Calcd., cc.	Bichromate Found. cc.	Error, cc.	H_2SO_4 of sp. gr. 1.84, cc.	Initial volume, cc.	Voltage break per 1 drop of reagent
1	48.26	48.25	−0.01	10	100	0.091
2	9.66	9.65	− .01	2	40	.175
3	9.66	9.65	− .01	2	40	.169
4	24.13	24.18	+ .05	5	50	.050
5	24.13	24.15	+ .02	5	50	.108

TABLE IV

TITRATION OF APPROXIMATELY 0.1 *N* BICHROMATE WITH FERROUS SULPATE

No.	Calcd., cc.	Ferrous sulfate Found, cc.	Error, cc.	E.m.f. difference, Pt vs. Au (a) Initial voltage	(b) Maximum voltage	(c) Break per drop of reagent at end-point
1	51.84	51.80	−0.04	0.203	0.495	0.287
2	25.92	26.00	+ .08	.220	.560	.340
3	10.36	10.35	− .01	.300	.505	.315
4	10.36	10.35	− .01	.293	.503	.313

From 2–10 cc. of sulfuric acid (sp. gr. 1.84) was present. Initial volume 100 cc. in no. 1 and 50 cc. in nos. 2 4.

Discussion

The **Pt-Au** system appears to be capable of use in solutions that are as dilute as 0.05 N.

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[2] Müller and Möllering, *Z. anorg. allgem. Chem.*, *141*, 111 (1924).

The general features of the graphs of the titration data are shown in Fig. 2. It will be noted that there is no pronounced peak in the curve for the titration of bichromate in hydrochloric acid solution, The very marked rise that is observed with sulfuric acid solutions appears to be a composite of the usual anomalous rise in potential at the Pt electrode[3] and the fall at the gold electrode. This was found to be true by following the changes at each electrode with the aid of an auxiliary reference electrode (see curves 3, 4 and 5, Fig. 2).

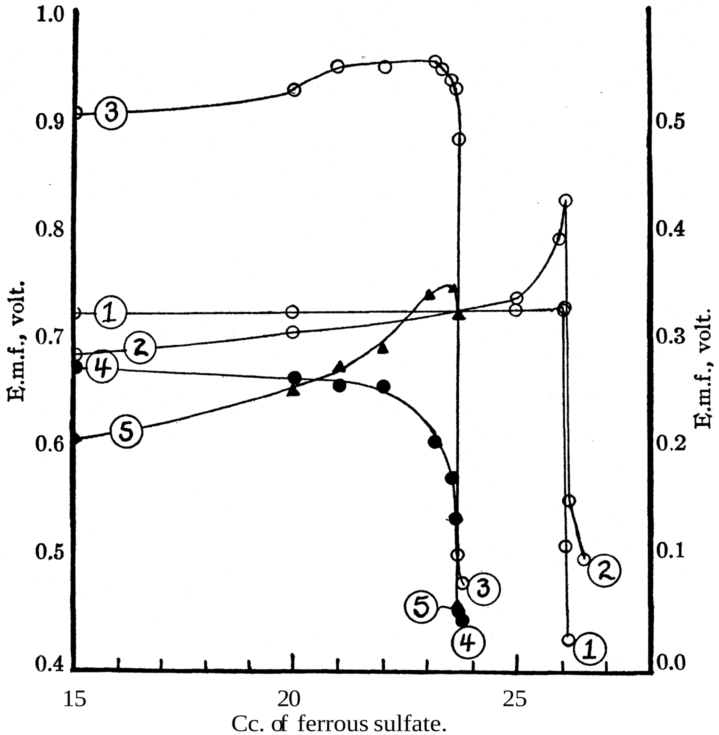

Fig. 2.—Titration of bichromate with ferrous sulfate (Pt-Au system). (Ordinates for 1, 2 and 5 at right; 3 and 4 at left.) Curve (1) 25 cc. of approximately 0.05 N bichromate titrated in hydrochloric acid solution. Curve (2) similar to (1) except that sulfuric acid was present. Curves (3, 4, 5) are from data of a single titration of 0.1 N bichromate with ferrous sulfate. (3) Pt-N. C. E. system. (4) Au-N. C. E. (5) Pt-Au system; (5) is a composite of (3) and (4).

The chief disadvantage of the Pt-Au system is the variable nature of the readings. The initial and maximum voltages show wide variations in magnitude for the same type of titration, so that it is difficult to judge

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[3] Forbes and Bartlett, THIS JOURNAL, 35, 1527 (1913).

the approach of the end-point or to predict the voltage range in which the end-point change will occur in any given case.

Summary

A brief study of the use of the Pt-Au electrode system has shown that it gives a sharp change in e.m.f. at the end-points of some oxidation-reduction reactions in 0.1 or 0.05 N solutions.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A SIMPLE CONTINUOUS READING METHOD OF ELECTROMETRIC TITRATION WITH BIMETALLIC ELECTRODES

BY N. HOWELL FURMAN AND E. B. WILSON, JR.

RECEIVED JUNE 18, 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

Electrometric methods of determining the end-points of volumetric oxidation-reduction reactions are accurate and convenient. Many varieties of systems have been developed to follow changes in the e.m.f. of a suitable pair of electrodes during the progress of a titration,[1] but not all of them possess the advantages of simplicity, economy of apparatus and speed. The system that is described in this paper combines these advantages and is, in addition, continuous reading.

Experimental

Apparatus.—The electrical system consists of a platinum electrode, a tungsten electrode,[2] a galvanometer and a high resistance that can be varied. The electrical connections are shown diagrammatically in Fig. 1. The platinum electrode was a wire of 0.33 mm. diameter (No. 28 B. and S. gage) and of 6–8 cm. length. The wire was soldered to a copper wire with gold; the platinum was sealed through the end of a glass tube (see Fig. 1). The end of the tungsten wire (No. 28 B. and S. gage; actual diameter 0.32 mm.) was dipped into the solution to a depth of 2–3 cm. The dimensions of the electrodes seem to have no very marked effect upon the behavior of the apparatus. A platinum wire of the size given seems somewhat more reliable than one of very small surface. The

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[1] For a review of these systems, see E. Müller, "Die Elektrometrische Massanalyse," 4th ed., Steinkopf, Dresden, 1926; I. M. Kolthoff and N. Howell Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, 1926.

[2] Qualitative studies have been made using tantalum, platinized platinum, copper or gold instead of tungsten. The Pt-Au system was the best of these combinations. It gave excellent end-point indications in the reaction between permanganate and ferrous sulfate but was, in general, far less sensitive than the Pt-W system.

electrodes must be clean. The solution should be effectively stirred (motor stirrer).

A handy resistance unit was assembled from inexpensive radio grid-leak mountings. The resistances were of the cartridge type, and were rated at 10,000, 18,000, 20,000 and 100,000 ohms.[3] By making one or two interchanges of resistors it is possible to vary the resistance in steps of about 10,000 ohms each up to 160,000 ohms. A resistance of about 50,000 ohms served for most titrations.

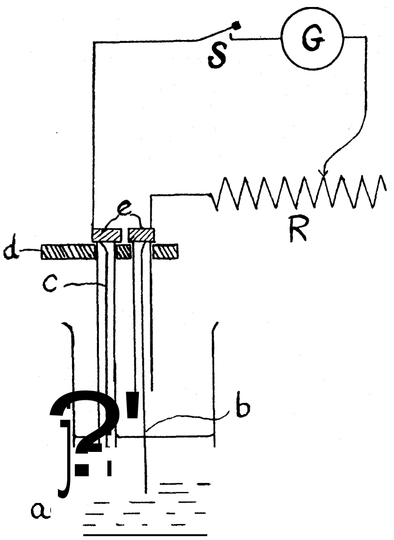

Fig. 1.—Apparatus. (a) Platinum electrode; (b) tungsten electrode; (c) copper wire. The copper and tungsten wires are wrapped around the glass tubes and held in place by the rubber tubes at (e); (d) is a Bakelite support for the electrodes. S, switch; G, galvanometer; R, variable high resistance.

The galvanometer was a Leeds and Northrup Company portable instrument (Type 2320D) of current sensitivity 0.5 micro-ampere. Any galvanometer of approximately similar characteristics should serve.

End-points.—Operation of the apparatus is very simple. The end-point is the largest single permanent deflection (usually 2–10 divisions) of the galvanometer that is produced by a single drop of the reagent, for all of the reactions that we have studied (ferrous sulfate-permanganate; ferrous sulfate-vanadic acid; ferrous sulfate-bichromate; iodine-thiosulfate). The galvanometer usually reads zero, or a low value, on the reducing side. As oxidizing agent is added, there is a slight increase in the galvanometer deflection. As the end-point is approached the needle gives temporary deflections that serve as convenient warnings. At the end-point there is a maximum permanent shift (2–10) divisions per unit volume of reagent. Further addition of oxidant produces relatively slight changes.

In the reverse titration there is a high initial galvanometer deflection, a maximum permanent downward shift in reading at the end-point and little further deflection on the addition of excess of reducing agent. Occasionally the end-point deflection is divided into two nearly equal parts. The maximum change per unit volume of reagent corresponds to the end-

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[3] The resistances were "Aerovox Lavite" resistors (Aerovox Wireless Corp., New York). A suitable unit can be assembled at a cost of $3 to $5. It was found that the resistors were in some cases as much as 10% higher than rated. We are indebted to Mr. W. S. Niederhauser for the resistance measurements.

point, as is the case in potentiometric procedures. Graphs with galvanometer readings as ordinates and cc. of reagent as abscissas are analogous to those obtained potentiometrically. In any case the end-point is definitely determinable by a slightly experienced operator.

Accuracy.—Approximately 0.1 or 0.05 *N* solutions of the reagents were prepared and standardized. Starch indicator was used in the iodine–thiosulfate reaction. In other cases the potentiometric method was employed. A large number of quantitative determinations were made for the ferrous sulfate–dichromate, ferrous sulfate–vanadic acid and iodine–thiosulfate reactions. In many of these titrations simultaneous observations were made by the potentiometric method and the new "galvanometric" method. The outstanding fact of such determinations was that in every instance the end-point determined with the galvanometer checked exactly with the potentiometer end-point; that is, the same drop of reagent produced the greatest relative change with both systems.

In order to determine whether the presence of the Pt-W system caused any change in the position of the end-point, determinations were made with the standard (Pt-N calomel) method alone. The errors thus found were no greater than the natural experimental errors; in fact, deviations from the average were as great for the standard method as for the galvanometer method.

Permanganate-Ferrous Sulfate Reaction

A preliminary orientation study showed that the Pt-W system gave excellent results. The galvanometer deflections at the end-points were large. There was, in every case, agreement with the usual potentiometric end-point.

Bichromate-Ferrous Sulfate

The solutions that were titrated contained 10–15 cc. of 12 *N* hydrochloric acid or 25 cc. of 6 *N* sulfuric acid in a total volume of 45–75 cc. Assuming that the average values obtained with the Pt-N calomel system were correct the errors found in the titration of 0.1 *N* bichromate were: +0.07, ±0.00, +0.04, +0.05, +0.06 cc. of 0.1 N ferrous sulfate. In these and subsequent determinations the amounts of solution that were pipetted out ranged from 10 to 50 cc.; the resistance was approximately 70,000 ohms. The end-point deflections per 0.05 cc. of reagent were 7–9 galvanometer divisions in hydrochloric and 3–5 divisions in sulfuric acid solution. In the reverse titration the errors found were: –0.04, +0.02, –0.06, ±0.00, ±0.00 cc. of 0.1 N bichromate. The end-point breaks were less pronounced than in the reverse titrations, being about 5 divisions in hydrochloric and about 4 in sulfuric acid solutions. The calculated cc. of bichromate are the average of three concordant determinations (Pt-N calomel).

The data for more dilute (0.05 *N*) solutions are presented in Tables I and II.

TABLE I

TITRATION OF FERROUS SULFATE WITH APPROXIMATELY 0.05 *N* BICHROMATE

	1	2	3	4	6	6	7
Bichromate, calcd. cc.	23.07	23.07	23.07	23.07	23.07	9.22	46.14
Bichromate found, cc.	23.10	23.03	23.09	23.09	23.11	9.27	46 18
Error, cc.	$0.03	−0.04	+0.02	+0.02	+0.04	+0.05	$0.04
Resistance, 1000-ohm units	58	58	40	100	50	58	58
Galvanometer defl. div. at end-point per 0.05 cc.	4.9	3.1	3.0	1.5	3	**3.9**	1.5

Acid present: Nos. 1, 2, 25 cc. of 6 N H_2SO_4; Nos. 3–7, 10–15 cc. of 12 *N* HCl. Initial volume, 50–65 cc.

Large variations in the resistance, therefore, do not change the order of magnitude of the sensitivity of the method.

TABLE II

TITRATION OF BICHROMATE WITH APPROXIMATELY 0.05 N FERROUS SULFATE

	1	2	3	4	5	6
Ferrous sulfate found (Pt-W), cc.	27.17	27.14	10.94	37.94	27.16	37.98
Ferrous sulfate found (Pt-N calomel)	27.17	27.14	...	...	...	...
Ferrous sulfate calcd.	...	...	10.86	37.99	27.16	37.99
Error, cc.	...	...	+0.08	−0.05	$0.00	−0.01

The general conditions were those of Table I except that the resistance was 58,000 ohms.

Unfortunately no independent comparisons of the bichromate and ferrous sulfate by the usual potentiometric method had been made within several hours of the time when these determinations were carried out. One of us (F.) made up solutions Nos. 3–6, and the other (W.) made the titrations without any knowledge as to the relative strengths of the solutions.

The Iodine-Thiosulfate Reaction.—The solutions were approximately 0.1 N.

TABLE III

TITRATION OF THIOSULFATE WITH IODINE (APPROXIMATELY 0.1 *N*)

	1	2	3	4
Iodine calcd., cc.	26.69	26.69	26.69	26.69
Iodine found, cc.	26.68	26.64	26.69	26.70
Error, cc.	−0.01	−0.05	±0.00	+0.01

The calculated values are the average of several concordant determinations with starch as indicator. The resistance was 86,000 ohms. The reverse titration was studied by simultaneous determinations with Pt-W, Pt-N calomel and starch. All three methods gave the same end-point within 0.05 cc. It is perhaps worth noting that in a few instances the electrical end-point by either system was a distinct fraction of a drop different from the color end-point. It appears that minute traces of iodine loosely combined with starch do not affect the electrodes as would free iodine. There appeared to be no immediate diffusion of iodine out of the complex, because the color remained faint blue while the potential was decidedly on the reducing side. The galvanometer deflections, per fraction of a drop of reagent at the end-point, were very large. Occasionally the change was distributed over two drops of reagent. The maximum rate of change per drop invariably checked with the potentiometer.

The Vanadic Acid-Ferrous Sulfate Reaction.—A 0.05597 N vanadic acid solution that had been standardized potentiometrically was used. The solution contained 30 cc. of sulfuric acid sp. gr. 1.84, per liter. In instances marked with an asterisk (*) the quantity of vanadic acid was unknown to the operator.

TABLE IV

TITRATION OF 0.05597 N VANADIC ACID WITH FERROUS SULFATE

	1	2	3	4*	5*	6*	7*
$FeSO_4$ calcd., cc.	28.76	28.76	28.76	28.76	11.61	11.61	11.61
$FeSO_4$ found, cc.	28.77	28.72	28.70	28.75	11.50	11.62	11.61
Error, cc.	+0.01	−0.04	−0.06	−0.01	−0.11	+0.01	±0.00

NOTE.—Some time elapsed between determinations No. 4 and 5, and the ferrous sulfate was restandardized. The resistance was 58,000 or 30,000 ohms. The initial volumes ranged from 35–50 cc., with either 6–10 cc. of concd. HCl, or 25 cc. of 6 *N* H_2SO_4 present.

The galvanometer deflections were the smallest per drop of reagent at the end-point of any case thus far investigated. The sensitivity was somewhat increased by dropping the resistance to 30,000 ohms.

Discussion

The chief possible source of error in this method seems to be the continuous production of current, which must occur at the expense of some reaction in the solution. Assuming that all of the current drawn is produced by the reduction of the oxidant (and this is not necessarily the sole source of current), and assuming that 10 galvanometer divisions represent 5 micro-amperes, it appears that this deflection could be maintained for one hour at the expense of about 0.05 cc. of 0.1 N reagent. Only a few minutes are required for the titration.

The relation of the potential difference between Pt-W and the difference between each wire and a N-calomel electrode is shown for a typical instance in Fig. 2. The slight current that is drawn does not affect the graph of the readings Pt vs. N calomel to any very considerable extent.

The authors have not thus far attempted to secure new evidence to establish the theoretical basis of the method. Analogous phenomena (persistent differences in oxidation potential) have been reported.[4] The gen-

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[4] Van Name and Fenwick, THIS JOURNAL, 47, 11 (1925).

eral characteristics of the Pt-W systems have been previously studied.[5] It is planned to study the behavior of the Pt-W system further to see how far polarization effects account for the phenomena observed, and to study this and other systems in conjunction with vacuum tube amplifiers. Preliminary experiment has shown that polarization effects due to grid current may play an important role in its application.

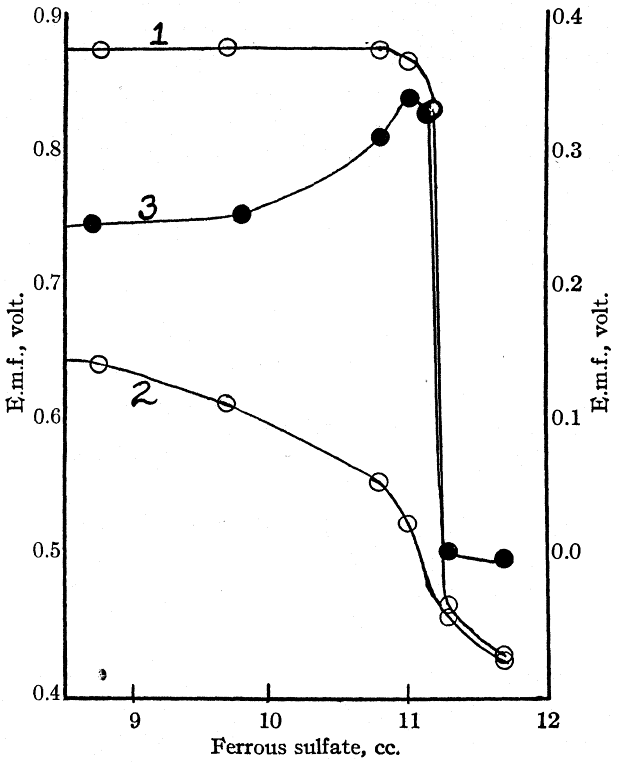

Fig. 2.—Titration of 0.1 *N* bichromate with ferrous sulfate. Ordinates for (1) and (2) at left. (1) Curve for Pt-N calomel, (2) for W-N calomel and (3) for Pt-W system, showing the sharp break at the end-point (ordinates of (3) at right of figure).

In the interactions between substances that are sufficiently far removed in the oxidation potential scale, there is a very close superficial analogy between the end-point indication in the present method and the excellent indication that is given by the method of Foulk and Bawden.[6] In the latter method, however, the high galvanometer readings are not always on the oxidizing side of the end-point.

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[5] Willard and Fenwick, This journal, 44, 2508 (1922).

[6] Foulk and Bawden, *ibid.*, 48, 2045 (1926).

The authors intend to study the application of the "Galvanometric" method to other reactions than those studied.

Summary

This paper describes a simple, direct reading and inexpensive system for determining end-points of oxidation-reduction reactions. The method depends upon the sudden change at the end-point in the potential difference between a platinum and a tungsten electrode which are immersed in the solution.

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

THEORY OF THE SORET EFFECT

BY E. D. EASTMAN

RECEIVED JUNE 22. 1927 PUBLISHED FEBRUARY 4, 1928

In a previous paper[1] a thermodynamic theory of the reversible Soret effect was given. It was there shown that the effect is related in magnitude to the heat of transfer of the constituents of the solutions in which it is manifested. Consideration of the nature of the latter quantity leads to a number of conclusions concerning general questions not yet experimentally settled. These inferences, and the views on which they are based, render intelligible many obscure features in this very uncertain field and offer guidance to further progress in it. They will, therefore, be outlined in this paper.

Definitions and Thermodynamic Relations

When a portion of one of the constituents of a solution is transferred by diffusion, or in the case of ions by an applied electric field, from one region to another within the solution, there is in general an accompanying absorption of heat from the surroundings of one region and evolution in those of the other. The quantity of heat absorbed from the surroundings of the region (of infinite extent) from which one mole of constituent **A** is transferred will be denoted by Q^*_A.[2] The entropy lost by the surroundings of the region from which the transfer is made is then $Q^*_A/T = S^*_A$. These quantities will be referred to as the heat and entropy of transfer, respectively. Their nature will be discussed in detail later.

In the former paper it was shown that in a binary solution placed in a temperature gradient the equilibrium compositions due to reversible effects are governed by the equation

$$(\partial \overline{F}_A/\partial N_A)_T\, dN_A = -\, S^*_A\, dT \tag{1a}$$

or

$$(\partial \overline{F}_A/\partial \ln N_A)_T\, d\ln N_A = -\, S^*_A\, dT \tag{1b}$$

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[1] Eastman, THIS JOURNAL, 48, 1482 (1926).

[2] In the previous paper, ref. 1, $\overline{Q}_A$ was used as the symbol for the heat of transfer. To avoid confusion with the partial molal quantities in the case of entropy it seems better to adopt the symbols above.

Here $\overline{F}$ and N represent partial molal free energy and mole fraction, respectively. These equations are correct if the composition change is the only effect produced by the gradient in temperature.

The first members of Equations 1 are each equal to the change in partial molal free energy of constituent A corresponding to an isothermal composition change of the same magnitude as that produced by the temperature gradient. It was this quantity which it was found desirable to use in defining a Soret coefficient for use in theoretical work. Calling the latter s_A, and writing $\mathrm{d}\overline{F}^*_A$ in place of the first member of (1) a defining equation may be written

$$s_A = \mathrm{d}\overline{F}^*_A/\mathrm{d}T = -\overline{S}^*_A \qquad (2)$$

In numerical comparisons of the effect in different solutions it is also desirable to employ where possible the coefficient defined by (2) rather than the ordinary ones (d ln $N_A/\mathrm{d}T$ or d ln $c_A/\mathrm{d}T$) resulting from direct determinations. The latter coefficients are proportional to the former in sufficiently dilute solutions, but in more concentrated imperfect solutions this proportionality fails. The magnitude of the composition change is then of lessened significance. As an extreme illustration of this the case of a metal, regarded as a "solution" of ions and electrons, may be cited. Ordinary temperature gradients can scarcely produce appreciable composition changes in such systems. Yet it would be a mistake to assume the Soret effect to be negligible, since an appreciable potential gradient and free energy difference are still possible. This is an example in which a large rate of change of free energy with composition is coupled with a small actual or fractional change in concentration. The reverse of this might be illustrated by substances forming a two-phase mixture. A solution near one of the equilibrium compositions would show very small values of $(\partial\overline{F}/\partial N)$ and correspondingly large values of $\mathrm{d}N$, even though the free energy change and therefore the true Soret effect were small.

To illustrate the difference in the two coefficients in solutions of some representative electrolytes, the following examples may be given. According to Arrhenius[3] d ln $c/\mathrm{d}T$ in 0.05 M copper sulfate is -2.2×10^{-3}, and in 0.5 M -9.3×10^{-3} deg.$^{-1}$ Using Lewis and Randall's[4] activity data, the corresponding values of s (Equation 2) are found to be -1.5 and -4.6, cal./deg., respectively. Chipman[5] gives -2.1×10^{-3} and -0.33×10^{-3} for the ordinary coefficient in 0.1 M and 10 M hydrochloric acid, while the values of s are 2.3 and 1.4 cal./deg. For most strong electrolytes in concentrations up to 0.1 M, however, the relative values of the two coefficients are constant within the present rather wide limits of error.

One further point concerning the application of Equation 2 to solutions

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[3] Arrhenius, *Z. physik. Chem.*, *26*, 18 (1898).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

[5] Chipman, THIS JOURNAL, 48, 2577 (1926).

of electrolytes should be mentioned at this stage. Solutions of binary electrolytes are really to be regarded in the present connection as systems of three components. This follows because of the partially independent distribution of the ions in the temperature gradient which manifests itself in the accompanying potential gradient[6] in the solution. It might, therefore, be supposed that the total Soret effect should be considered in two parts. These parts would be associated, respectively, with the free energy change due to the concentration gradient and that due to the electrical gradient. The latter part of the effect may, however, be seen to be negligible compared to the first. Owing to the very strong forces between ions of opposite charges, the gradient in ionic composition must be extremely small. The number of equivalents of positive ion transferred in establishing equilibrium, or in returning to the normal condition after removal of the temperature gradient, is therefore almost exactly the same as that of the negative ion. The free energy difference per mole of either ion transferred in such diffusion, which is the product of the difference in number of equivalents of oppositely charged ions, and the potential difference between which they are moved, must be negligibly small even though the potential difference itself is not. This being the case, the Soret free energy difference is due mainly to the concentration difference of the electrolyte and is governed by an equation like *(2)* in which the entropy term is the sum of the entropies of transfer of the ions corresponding to one mole of electrolyte. That is, the system may still be treated as one of two components.

The Nature of Heats of Transfer in Solutions of Electrolytes

For the purposes of the present discussion the space in the vicinity of an ion in an undissociated polar solvent may be divided, roughly, into three concentric regions of gradually differing properties. First, there is the "ion-cavity,"[7] within which there are no solvent molecules. This space varies in size from case to case and appears to be large compared to the volumes defined by the outer electron orbits of the ion. Immediately outside of the ion cavity the (polar) molecules of solvent are strongly attracted and oriented. The inner layers of solvent molecules in this second region, and those extending out from it to varying distances in different cases, are held so strongly by the central ion as to form a complex with it, acting in processes of diffusion, as a single molecule. The third region comprises all the rest of the outer space. In this sphere the solvent molecules are still subject to forces of compression and orientation, diminishing with distance from the center of the complex, and not sufficiently strong to bind these molecules to the ion. The second and third

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[6] Potential gradients of this kind are discussed in the paper following this.

[7] Webb, THIS JOURNAL, 48, 2689 (1926).

of these regions obviously merge into each other in such a way as to prevent sharp boundaries from being drawn between them.

When a solvated ion of the kind described is transferred by diffusion from one region to another of the solvent, the aggregate comprising the first and second regions above remains mostly intact and takes part in no internal energy or entropy changes. But as the ion moves it leaves behind material which had been under its influence in the third sphere, and brings under its influence solvent molecules not previously so strongly affected. A relaxation occurs, therefore, in the region from which it goes, with an attendant increase in entropy and absorption of heat. The reverse effects appear in the region into which it moves. It is, therefore, these changes in the third sphere that give rise to the heats of transfer that determine the reversible Soret effects in solutions of ionized substances.

The conception of solvated ions outlined above takes into account only the electrical effects produced by the charge of the ion upon the molecules of the solvent regarded as electric dipoles. The mechanism of the heat of transfer dependent upon it holds strictly therefore only in the simpler cases. Several factors that were neglected in its discussion may be of importance in certain cases. Any sort of chemical bonding in the ion aggregate may greatly affect the spheres of influence about the central charge, and so alter the heat effects attending its diffusion. This kind of thing may differentiate, for example, between positive and negative ions in their orienting and bonding effects on water molecules. The hydrogen nuclei of the solvent may form a sort of hydrogen bond[8] with electrons of the outer shell of negative ions, a type which is not possible between the oxygen atoms and most positive ions. The effect of such bonds, if extensively formed, would be to increase region two at the expense of three, with consequent lessening of the heat of transfer. The possibility that either ion of the solvent may be transferred, in effect, by a chain mechanism, must also be considered in solutions of acids and bases. For if this occurs, not only the energy represented in the third sphere above, but that of the second as well, a very much larger quantity, would be involved in the heat of transfer.

The simple mechanism pictured above would appear to afford a basis for quantitative theoretical treatment. The entropy effects in region three about the ion depend upon the degree of compression and orientation of the solvent molecules in it. Both are approximately calculable in any element of volume at a given distance from an ionic center by methods like those of Webb.' The dependence of the entropy of the solvent upon pressure is measurable, and the entropy change due to orientation might be calculated from the relative probabilities of the axial distributions

[8] Rodebush and Latimer, THIS JOURNAL, 42, **1419 (1920).**

of the dipoles in the field of the ion and without it by methods like those of Langevin. Volume integrations throughout the sphere should result in the desired entropy. One of the limits in the integration is obviously infinity. The other, which is the boundary between regions two and three, is somewhat indefinite and variable from one ion to another. It could probably be fixed with enough exactness as the radius at which the equipartition amount of kinetic energy would be just sufficient to carry a solvent molecule against the force of attraction of the ion (known as a function of distance) to infinity. This would be, on the average, the dividing line between the "bound" and "unbound" solvent molecules, and would serve to define the third region above for the purpose of integration. The calculation outlined therefore appears theoretically feasible. Practically, however, several obstacles are encountered. Thus some of the essential data required in it, such as the electric moment of solvent molecules, are known only very inaccurately at present. Further refinements, taking into account the ion cavity, in calculations of the force field about ions, and some indication as to the influence of other factors than the purely electrostatic ones, are no doubt also necessary. This is particularly true since the effect in question is of the second order, as compared with the entire "entropy of solvation" of the ions. The actual application must therefore await these developments. It is, however, possible to draw a number of conclusions and suggest correlations from these ideas. Before proceeding to their discussion it is desired to present in the next section a comparison of certain indirectly measured entropies of transfer with those corresponding to measured Soret effects.

Comparison of Directly and Indirectly Determined Soret Effects

In the paper following this, approximate values are calculated for the entropy of transfer of the ions of a number of substances for which Soret coefficients have also been measured. The Soret coefficients corresponding to these, together with the experimentally determined values by several investigators, are shown in Table I.

TABLE I

SORET COEFFICIENTS, IN CALORIES PER DEGREE PER MOLE, OF CERTAIN ELECTROLYTES IN WATER

Observer	Av. temp., °C.	Av. concn., *M*	HCl	LiCl	NaCl	KCl	NH_4Cl
Soret[g]	47	±1.0	...	−0.10	−0.67	−1.1	..
Arrhenius[3]	47	0.02	−2.9	....	−1.3	....	..
Wereide[10]	50	.17	...	....	(−2.5)	....	..
Chipman[5]	25	.1	−2.3	−0.023	−0.15	−0.19	0.00
Calculated	25	.02	−9.3	−0.1	−0.9	−1.0	0.0

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[9] Soret, *Ann. chim. phys.*, [5] 22, 293 (1881).

[10] Wereide, *Ann. Physik*, 2, 55 (1914).

The calculated values in the last line of Table I are approximate in character and subject to revision when more reliable measurements of the electromotive forces from which they were obtained are available. They are, however, thought not to be seriously in error. In comparing them with the experimental Soret coefficients of the table it is seen that they agree fairly well with the older determinations, but are much higher than the more recent results of Chipman. It should be borne in mind in this connection that for stable substances all of the systematic errors of measurement render the observed values too low. There is, moreover, much evidence that some unstudied source of error is present in some, at least, of the measurements. Thus, two observers of the same quantity seldom agree. Duplicate determinations by one observer ,show differences much larger than the apparent errors in either observation. The occasional occurrence of curves of Type C in Chipman's[5] observations of the approach to equilibrium points to the presence of convection, the effects of which may have been present but masked in his other experiments. The relative values obtained by a single observer for a series of substances are probably approximately correct. It is only to such relative values that much weight is given in the following discussion, since it appears to the writer that few actual magnitudes for individual substances are known at present with any degree of certainty. It is also thought that the indirect method of determination is capable of greater accuracy than the direct.

Effect of Concentration on Magnitude of Soret Coefficients

The mechanism outlined in the second section to explain the heat of transfer of ions obviously requires a finite value of this quantity for every ion at infinite dilution. As has been previously assumed, and will be discussed later, in strong electrolytes the total effect is the sum of the effects of the constituent ions. For this class of substance it follows that the Soret coefficient approaches a constant finite value with dilution.[11] The form of the curve chosen by Chipman[5] to represent his results for hydrochloric acid at small concentrations is therefore correct.

The heat and entropy of transfer have many of the properties of partial molal quantities. It is easy to show, for example, that for both quantities equations of the following type are valid.

$$N_A S_A^* + N_B S_B^* + \ldots\ldots. = 0 \qquad (3)$$

It follows, therefore, that in the infinitely dilute solution the Soret effect (defined by Equation 2) is zero for the solvent though it is not for the solute; and dN/dT becomes zero for both.

In solutions of electrolytes each ion is surrounded mainly by ions of

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[11] **This corrects a statement in the earlier paper. See also in this connection Rodebush, THIS JOURNAL, 49, 792 (1927), and Eastman, *ibid.*, 49, 794 (1927).**

opposite sign. The decrease in average distance between oppositely charged ions produced by increasing concentration from infinite dilution will, up to a certain limit at least, increase the field acting on the intervening molecules of the solvent and therefore increase the heat of transfer and Soret coefficient. With further approach of the oppositely charged centers, conditions become more complex and it is difficult to be sure without exact analysis how the third zone of the ions will be affected. If there is appreciable formation of ion pairs, with partial neutralization of the external fields of the ions, a decrease in heat of transfer may be looked for. This would lead to a maximum in the Soret coefficient at higher concentrations. In certain cases, as is pointed out in the following section, continued increase in concentration may lead to a reversal of sign of the effect, with the possibility of a minimum as well as maximum.

The Sign of the Soret Effect

As long as the charge of the ion is chiefly responsible for its solvation, the entropy of transfer of strong electrolytes predicted on the basis of the above mechanism will always be such as to produce an increased concentration of solute in the colder portions of the solution. This is found experimentally to be the case.

It would appear possible, however, to find solutions in which the role of ionized solute and polar (un-ionized) solvent might be reversed at different concentrations. For example, a small amount of water in hydrogen chloride might be ionized and solvated by the halide molecules. It should then be the water which would show increased concentration at the lower temperature. It might, of course, in this instance be necessary to go to very great dilution to secure much ionization of the water. Two constituents of more nearly equal ease of ionization in solution, and still ionized but little when pure, might more readily show this behavior.

Additivity of Soret Coefficients of Ions

The present theory requires, as does almost any other, that individual values be assignable to the Soret coefficients of all ions at infinite dilution, irrespective of the particular combination, and this idea has been used throughout. The theory also indicates many specific effects (such as the possibility of different geometrical packing of ions of different size ratios) which might destroy the additivity in more concentrated solutions. None of these effects would be thought, however, to be of great importance below about 0.1 *M*. That the additivity rule has not been approximately established experimentally at these concentrations is a further indication of uncertainty in the magnitude of the experimental values.

Correspondence with Mobilities of Ions

The total entropy of hydration of ions is known[12] to be an approximately linear function of the inverse of the radius of the ion. The entropy located in the outer sphere of unbound solvent molecules probably is a similar function of the radius of the ion complex (second sphere). The mobility of the ion may also be expected to be a similar function of the latter quantity. If it is, the Soret coefficient of ions should form a series having about the same order as the mobilities. The experimental values again are too uncertain to permit sure conclusions. Yet it appears that in certain series of similar ions, alkalies and halides, the order is actually the same. Apparently the generalization cannot be extended to ions of dissimilar type. For example, ammonium ion and, if the calculations of the following paper are correct, chloride ion appear to have much lower Soret coefficients than potassium ion, though the mobilities are not greatly different. The former both belong to the class of ions in which the electrical effects are perhaps not the only ones determining the size of the ion complex, which may account for the discrepancy.

Effects in Solutions of Non-electrolytes

In considering non-electrolytes in the light of the discussion in the second section, it is apparent that any kind of a molecule that can influence the neighboring molecules of the solvent must give rise to a finite Soret effect, even at infinite dilution. The fields of molecules of non-electrolytes are very much more nearly closed or saturated than are those of ions. The reversible Soret coefficients of non-electrolytes in general should then be very much smaller than those of ions. Even in the latter the effect is often small. With all non-polar substances and many non-electrolytes the coefficient may then be expected to be in general very close to zero. This is found experimentally by Wereide[10] and others to be true for a number of typical substances. Those for which the values appeared not to be zero are almost without exception of an unstable type in which some reaction occurring at different speeds at different temperatures might cause spurious effects. As an example, the fermentation of unsterilized sugar solutions may be mentioned. It is, of course, possible that extremely polar molecules may give rise to effects comparable with actually dissociated ions. In the absence of such polar bonds the conclusion seems fairly sure that only very small reversible Soret coefficients are possible.

Reversibility of the Effect

In the former paper the question of the relative magnitude of the reversible and irreversible Soret coefficients was left open. It now seems

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[12] Latimer and Buffington, THIS JOURNAL, 48, 2297 (1926).

likely that in liquid solutions only the reversible effect is of importance. The conditions favorable to a large irreversible effect would appear to have been met in several of the solutions of non-electrolytes which have been studied. The failure to obtain measurable effects (in cases where the source of error mentioned above was precluded) indicates that no large irreversible effect exists in these solutions.

Summary

In this paper the thermodynamic properties of the entropy of transfer of dissolved substances are discussed. This quantity is also considered in its relation to the effect on the solvent of the charge of the ions of electrolytic solutes. A comparison of indirectly determined entropies of transfer is made with measured Soret coefficients for certain substances. From these three sources a number of conclusions, often to be regarded as predictions for the guidance of further experimental investigation but all of a high degree of probability, are drawn. The following ideas are in this way developed.

Soret coefficients are best expressed, when possible, in terms of entropies of transfer. A solution of an electrolyte may be considered from the standpoint of the Soret effect as a two-component system in spite of the partial separation of positive and negative ions in the temperature gradient. Some unknown source of error probably affects seriously many of the existing measurements of Soret coefficients, and indirect determinations may prove more reliable. The Soret coefficient of the solute in imperfect solutions is finite at zero concentration and nearly constant over a certain range from zero. At higher concentrations of strong electrolytes an increase in magnitude of the effect is normally expected. The possibility, in some instances, of a change in sign with both a maximum and minimum in the curve against composition is indicated. The coefficients for all strong electrolytes at small concentrations in water are negative in sign. The Soret coefficients of ions are additive. There is a limited correspondence between the mobility of ions and their Soret coefficients. The Soret coefficient in solutions of non-polar substances is negligibly small, as is also the irreversible Soret effect in all liquid solutions.

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

ELECTROMOTIVE FORCE OF ELECTROLYTIC THERMOCOUPLES AND THERMOCELLS AND THE ENTROPY OF TRANSFER AND ABSOLUTE ENTROPY OF IONS

BY E. D. EASTMAN

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Systems of the type represented schematically as follows **are** often referred to as electrolytic thermocouples

$$\underset{T_1}{\text{Electrode}},\ \underset{T_1}{\text{Solution I}},\ \underset{T_2}{\text{Solution II}},\ \underset{T_1}{\text{Solution I}},\ \text{Electrode} \qquad \text{(I)}$$

The two electrodes in this arrangement are identical and are kept at the same temperature. Solutions I and II, the junctions of which are at different temperatures, may contain the same electrolyte at different concentrations, or different electrolytes.

Other arrangements consisting of two similar electrodes, at different temperatures, and a single solution in which the temperature gradient lies, are also occasionally given this name. The latter type may be represented as follows:

$$\underset{T_2}{\text{Electrode}},\ \text{Solution},\ \underset{T_1}{\text{Electrode}} \qquad \text{(II)}$$

In a previous paper[1] arrangements like (II) were referred to as thermocells. To distinguish them from the first class, this designation will be continued here.

The electromotive force of these cells is related to the entropy of transfer[2] and partial molal entropy of the ions of the electrolytes. Of the latter quantities, the first is of interest in connection with the Soret effect and the second is capable of many applications in the thermodynamics of solutions. It is the purpose in this paper to show the thermodynamic relations between these quantities and to employ certain of the existing data in illustrative calculations in order to determine to what extent it may prove possible to utilize these methods in numerical evaluations.

Thermodynamic Relations

Electrolytic Thermocouples.—The cells of Type I to be utilized in the later calculations all involve solutions of uni-univalent electrolytes having a common anion. The theory outlined will, therefore, be restricted to this case, though it is readily generalized. It is also convenient to consider cells in which the temperature difference is infinitesimal, T_1 and T_2 of Arrangement I being replaced by T and $T + dT$.

When one faraday of electricity is passed through systems of this kind, the direction of positive current being from left to right through the cell,

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[1] Eastman, THIS JOURNAL, 48, 1482 (1926).

[2] For a discussion of this quantity, see the preceding paper.

the change in state produced may be considered in the following parts: A, the electrode reaction at the first electrode, occurring at temperature T; B, the change, or "reaction' at the liquid junction, at T; C (1), the transfer of t_{C_2} equivalent of the cation of solution II from T to $T + dT$ and (2) the corresponding transfer at t_{A_2} equivalent of anion from $T +$ dT to T (t with the appropriate subscripts being used to represent the transference numbers of the ions in the two solutions); D, the reaction at the liquid junction at T + dT; E (1), the transfer of t_{C_1} equivalent of positive ion in Solution I from T + dT to T; and (2), the transfer of t_{A_1} equivalent of negative ion from T to T + dT; F, the electrode reaction, reversing (A) above, at T.

The electromotive force, dE, corresponding to this series of changes, may be shown by the methods of the earlier paper to depend upon the heat transferred by reversible absorption at the upper temperature and evolution at the lower. The relation is

$$FdE/dT = L/T = AS \tag{1}$$

Here F is the equivalent of electricity, and L and A S are the heat absorbed from and entropy lost by the surroundings of the system at the upper temperature and transferred to the lower when one faraday is passed reversibly from left to right through the cell.

Regarded from the standpoint of heat transfer in the cell processes, it is obvious that the electrode reactions, items A and F above, are without effect. The liquid boundary reactions, B and D, do, however, produce a heat transfer. The attendant entropy effect (loss by surroundings or gain by system due to the reaction at the upper temperature) will be called ΔS_B.

There is also an entropy effect due to the transfer (items C and E) of the ions between the two temperatures. The net entropy of transfer of the ions (loss of entropy by the surroundings at T + dT and gain at T) will be called AS*.

Considering the two effects above, Equation 1 may be rewritten as

$$FdE/dT = \Delta S_B + AS^* \tag{2}$$

The temperature coefficient of the whole cell as given by (2) may therefore be considered in the separate parts indicated. The part which may be designated $dE_B/dT = \Delta S_B/F$, due to the liquid junctions, may be calculated (exactly at infinite dilution and approximately at finite concentrations) by the methods due to Nernst and Planck. The remaining part, $dE^*/dT = \Delta S^*/F$, due to the transfer of the ions between different temperatures, may then be obtained from the measured e.m.f. of the cell and the calculated change in junction potential. This corrected e.m.f. may then be related to the entropies of transfer of the individual ions, since ΔS^* is expressible in terms of them. Thus, if S^* is the molal entropy of transfer of a single ion,

$$\Delta S^* = t_{C_1}S^*_{C_1} - t_{C_2}S^*_{C_2} + (t_{A_2} - t_{A_1})S^*_A \tag{3}$$

It will also be observed that $\mathrm{d}E^*/\mathrm{d}T$ is the potential gradient accompanying the thermal one, and is due no doubt to partial separation of positive and negative ions in the solution lying in the temperature gradient, as first suggested by Nernst.[3]

Throughout the preceding discussion the composition of the electrolytes in the temperature gradient has been assumed to be uniform. Equations 1, 2 and **3** are exactly valid only if this condition is fulfilled, and do not apply, therefore, to cells in which Soret equilibrium has been established. Other equations covering the latter case can be deduced. The Soret equilibrium is, however, established very slowly as compared with the other cell processes, and it is possible therefore to avoid its effects by proper experimental precautions. It is then permissible to apply the equations in the forms given above.

Thermocells.—Cells of Type II were specifically treated in the former paper.[1] The entropy of transfer of the ions was neglected, however, in the development given there. When this is included, the equation (19 of the former paper) becomes

$$F\mathrm{d}E/\mathrm{d}T = \Delta S_R + AS^* \tag{4}$$

In this equation ΔS_R is the entropy gained by the system at the higher temperature in the electrode reaction caused by one faraday passing from left to right through the cell. AS*, again the net entropy of transfer of ions, is now given by

$$AS^* = t_C S^*_C - t_A S^*_A \tag{5}$$

The Soret effect is again neglected, since the measurements may be made so as to exclude its influence in the solution, and it is assumed to be negligible for the electrons in the wire in the temperature gradient.

By opposing two cells of this second type having the same electrodes, and electrolytes with a common negative ion but with different positive ions, a change in state is produced on operation which is the same as that in the Type I cells, except for the liquid junction reactions. These combinations without liquid junction obviously offer many advantages over the first type for the determination of entropy sums such as that in Equation **3.**

Approximate Calculation of Entropy of Transfer of Ions

Of the existing data applicable in Equations 2 and **3** for the determination of entropy of transfer of ions, the most satisfactory are those of Podzus,[4] since they relate to dilute solutions and were obtained under conditions designed to eliminate the effect of the Soret phenomenon. The observations to be used here were obtained from a series of cells of Type I (and a few combinations of Type II) in which the first and second electrolytes

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[3] **Nernst,** *Z. physik. Chem.*, **4**, 129 (1889).

[4] **Podzus,** Ann. *Physik*, [4] **27,** 859 (1908).

were different members of a group comprising the chlorides of hydrogen, ammonium and four of the alkali metals. They may be cast in the form of five independent equations, based upon Equation 3, as follows

$$
\begin{array}{lr}
0.497\,S^*_{\mathrm{K}^+} - 0.822\,S^*_{\mathrm{H}^+} - 0.325\,S^*_{\mathrm{Cl}^-} = -7.15 \pm 0.15 & (6)\ \mathrm{a} \\
0.497\,S^*_{\mathrm{K}^+} - 0.343\,S^*_{\mathrm{Li}^+} + 0.154\,S^*_{\mathrm{Cl}^-} = 0.57 \pm 0.15 & \mathrm{b} \\
0.497\,S^*_{\mathrm{K}^+} - 0.402\,S^*_{\mathrm{Na}^+} + 0.095\,S^*_{\mathrm{Cl}^-} = 0.08 \pm 0.1 & \mathrm{c} \\
0.497\,S^*_{\mathrm{K}^+} - 0.508\,S^*_{\mathrm{Rb}^+} - 0.011\,S^*_{\mathrm{Cl}^-} = -0.07 & \mathrm{d} \\
0.497\,S^*_{\mathrm{K}^+} - 0.498\,S^*_{\mathrm{NH}_4^+} - 0.001\,S^*_{\mathrm{Cl}^-} = 0.60 \pm 0.1 & \mathrm{e}
\end{array}
$$

The directly observed data upon which these equations depend are average temperature coefficients of electromotive force, dE/dT, over intervals of about 20°, the mid-point being 25°. The concentration of the solutions was 0.02 N. Podzus' calculations from the Planck equation of the junction e.m.f.'s were used to correct the direct observations to give the values of ΔS^*. The numerical values of ΔS^* in Equations 6 are averages obtained from several combinations. The average deviation of separate values from the mean is indicated in the equation when more than one value is obtainable.

From thermodynamics alone these relations are all that can be obtained. To calculate the entropies of transfer of the individual ions some further relation between them is required. At the present time no such relation is known. In the paper preceding, however, certain general deductions of a qualitative character were made concerning the magnitudes of these quantities. Thus it was concluded that they are independent of each other in dilute solution and that they are always positive in sign. It also appears probable that in a series of closely related ions, such as those of the alkali metals, the entropies of transfer vary in the same order as the mobilities. Utilizing these ideas in connection with Equations 6, the magnitudes may be roughly fixed for each ion. Thus from Equation 6e the minimum value of $S^*_{\mathrm{K}^+}$ is determined to be about 1.2 ± 0.2, since neither $S^*_{\mathrm{NH}_4^+}$ nor $S^*_{\mathrm{Cl}^-}$ may be less than 0. From Equation 6c, the maximum value of $S^*_{\mathrm{K}^+}$ is fixed as 0.9 ± 1, since $S^*_{\mathrm{Na}^+}$ cannot (according to the above ideas), exceed $S^*_{\mathrm{K}^+}$ and $S^*_{\mathrm{Cl}^-}$ cannot be less than 0. Adopting 1.0 as a probable value of $S^*_{\mathrm{K}^+}$, that for $S^*_{\mathrm{Cl}^-}$ must be about 0.0 if Na^+ is to fall between Li^+ and K^+ in the series. With these values fixed, the others follow from the equations. The experimental errors in ΔS^+ in Equation 6 are large enough to render these values rather uncertain. Within the limits of error, however, the values shown in Table I agree with the experimental data, and with the general properties enumerated above, and no large changes in them are possible without some departure from this agreement.

TABLE I

ENTROPY OF TRANSFER, IN CALORIES PER DEGREE PER MOLE, OF IONS IN 0.02 N SOLUTIONS AT 25°

Ion	H^+	Li^+	Na^+	K^+	Rb^+	NH_4^+	Cl^-
Entropy of transfer	9.3	0.1	0.9	1.0	1.1	0.0	0.0

The values in Table I can scarcely be said to have been calculated. Rather, they have been selected to agree with the known data and probable laws. Nevertheless, they can hardly fail to be correct in order of magnitude and the probability is high that the relative and absolute values are roughly correct also. Due in part to experimental uncertainties and partly to the approximate character of the assumptions made, nothing more than this rough correspondence can be claimed. The results of these estimates make it appear probable that experiments more expressly designed for the purpose would lead to a fairly close limitation of the values of the entropies of transfer, even though a sufficient number of quantitative relations for their exact determination be not available.

The results of the application of the values in Table I to the calculation of Soret coefficients are discussed in the preceding paper.

Partial Molal **Entropy of** Chloride Ion

Richards[5] measured dE/dT in cells of Type II exemplified by

$$\underset{T_2}{Hg},\ \underset{T_2}{HgCl},\ HCI(O.l\ M),\ \underset{T_1}{HgCl},\ \underset{T_1}{Hg}$$

Applying Equation 4 to this cell, it is seen that ΔS_R is the entropy change in the reaction

$$Hg + C1^-(0.1\ M) = HgCl + E^-_{(Hg)}$$

Further

$$AS^* = t_H S_H^* - t_{Cl} S_{Cl}^* \qquad (7)$$

Using the measured values of dE/dT, with the entropy of transfer of H^+ and Cl^- from Table I, the entropy change in the calomel electrode half reaction may be calculated. From the known entropy of calomel and mercury that of chloride ion may then be obtained.

Richards's best experiments were made with the chlorides of hydrogen, lithium, sodium and potassium as electrolytes. Data pertaining to each of these cells are collected in Table II. The total entropy change of the cells as calculated from dE/dT is shown in the second column of the table. The temperature to which it corresponds is 15°, and the concentration of electrolyte is 0.01 M. The third column gives AS^* as calculated by Equation 7 from the data of Table I. The latter apply to 0.02 M solution at 25°. In calculating ΔS_R in the fourth column, the errors due to these differences in concentration and temperature are assumed to be no larger than the other errors. It is also assumed that the Soret equilibrium was not established in the cells, though this assumption is difficult to verify from Richards's descriptions. The entropies of Hg and HgCl used, with ΔS_R, in calculating $\overline{S}_{Cl^-}$ in the fifth column of the table are 17.8 and 23.2, respectively.[6]

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[5] Richards, *Z. physik. Chem.*, **24**, **39** (1897).

[6] *See* Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, and Gerke, THIS JOURNAL, **44, 1684 (1922).**

TABLE II

PARTIAL MOLAL ENTROPY, IN CALORIES PER DEGREE, OF CHLORIDE ION IN 0.01 M SOLUTION AT 15°

Electrolyte	FdE/dT	AS*	ΔS_R	$\bar{S}_{Cl^-}$	Deviation from av.
HCl	−15.2	7.6	−22.8	28 2	0.2
LiCl	−23.1	0.0	−23.1	28.5	.5
NaCl	−21.9	.4	−22 3	27 7	.3
KCl	−21.7	.5	−22 2	27 6	.4
Average			−22 6	28 0	.4

A set of observations similar to those of Table II but with 0.1 M electrolytes gives 24.5 as the average entropy of chloride ion, at this concentration and 15°, the average deviation of individual results from the mean being 0.5. These values of $\bar{S}_{Cl^-}$ are in close agreement with those calculated by Chipman.[7]

In spite of the lack of correspondence of temperature, concentration and other experimental conditions in the various measurements on which these calculations are based, they appear to be of sufficient reliability to indicate the possibilities of this method of determination of partial molal entropies of ions. Absolute values for individual ions, as obtained here, are unnecessary in ordinary thermodynamic work, yet their use would agree with usual practice when pure substances are concerned. Comparison of these values with those calculated in other ways[8] is also of some interest. For these reasons this field seems worthy of further experimental development.

Summary

Thermodynamic equations are given connecting the entropy of transfer ions and entropy changes in single electrode reactions with the e.m.f.'s certain thermo-electric cells. Application of them is made to the calculation of the entropy of transfer of six of the common univalent cations, and chloride ion. As an illustration of the possibilities of the method in the field of ionic entropies, the partial molal entropy of chloride ion is calculated.

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[7] Chipman, *Thesis*, University of California, 1926. Chipman made the assumption in his work that the potential gradient (corresponding to AS*) in solutions of lithium chloride and ammonium chloride is negligibly small. This was based in turn on an assumed connection between the potential gradient and the Soret effect, the measured values of the latter being very small in the solutions in question. These ideas are supported by the present calculations.

[8] See, for example, Latimer, THIS JOURNAL, 48, 1234 (1926).

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

OBSERVATIONS ON THE RARE EARTHS. XXVI. THE PURIFICATION AND ATOMIC WEIGHT OF ERBIUM

BY ARTHUR EVAN BOSS WITH B. S. HOPKINS

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Introduction

The object of the work described in this paper was to continue the purification of erbium material and to determine the atomic weight of erbium by using the chloride-to-silver ratio.

The accepted value for erbium is based on the work of Hofmann[1] on the oxide-to-sulfate ratio. The average of three determinations gave the value 167.68.

In 1917 Wichers, Hopkins and Balke[2] prepared erbium material of high purity and attempted to determine the oxide-to-chloride ratio. They found that the oxide, which they prepared by ignition of the oxalate, retained notable quantities of carbon dioxide, even after ignition at a temperature just below 900° for ten hours.

Sources of Material

The material used in the study of this element came from two different sources (1) Texas gadolinite and (2) Series M (bromates).

This material had been treated as described by Driggs and Hopkins[3] until fractions could be removed which showed only yttrium and erbium, and which were well removed from those fractions containing holmium on the one hand and thulium on the other. The material in the final fractionation series showed no indications of the presence of any rare earths other than yttrium and erbium. This yttrium-erbium material had been further purified by being run as a nitrate fusion series by F. H. Driggs.

Separation of Yttrium and Erbium

The nitrate fusions were continued, using the furnace built by Driggs and Hopkins for the purification of holmium.[3] After some fifty further fractionations, the four head fractions, on analysis by the permanganate method of Gibbs,[4] showed values which were alike within the limits of experimental error. This close agreement of equivalent weights must be taken as evidence of the removal of yttrium. The arc spectrum of erbium is not sufficiently well mapped to be useful in determining the purity. The observation of the magnetic susceptibilities, as used by Driggs and Hopkins to show the absence of dysprosium from their holmium, is much

[1] Hofmann, *Ber.*, 43, 2631 (1910).

[2] Wichers, Hopkins and Balke, THIS JOURNAL, 40, 1615 (1918).

[3] Driggs with Hopkins, *ibid.*, 47, 363 (1925).

[4] Gibbs, *Am. Chem. J.*, 15, 546 (1893).

less sensitive in the case of an erbium-yttrium mixture than is the determination of the equivalent weight.

Since Wichers, Hopkins and Balke found that the method of partial precipitation with sodium nitrite gave a rapid separation of yttrium and erbium, some of the yttrium-rich ends of the nitrate fusion series were taken, combined and subjected to fractionation with sodium nitrite. In this way practically pure yttrium material was separated at the one end of the series and erbium material at the other. The two head fractions, 8D and 8E, were taken for analysis.

Preparation of the Reagents for Atomic Weight Study

The purification of the reagents in this investigation was carried out in the same manner as described in earlier publications of this Laboratory.[5]

The erbium nitrate obtained from the fractions 18, 19, 17, 8D and 8E was purified by alternate precipitations as oxalate and hydroxide, the second hydroxide and the second oxalate precipitation being from conductivity water. The final oxalate from each fraction was dried and ignited to the oxide in a platinum crucible.

The anhydrous chloride was formed under the conditions described by Wichers, Hopkins and Balke.

Ratio of Erbium Chloride to Silver

The ratio of erbium chloride to silver was determined in essentially the same manner as described by Driggs and Hopkins on the atomic weight of holmium.

In the following tabulated data the number of the fraction from which the material was taken is shown, together with the weight of the anhydrous chloride, the weight of silver necessary and the atomic weight of erbium. The number in parenthesis shows the determination in which the material had been previously used.

The weighings were made by the method of substitution, the tare flask being of quartz and differing from the reaction flask by only a few milli-

TABLE I

RESULTS OF DETERMINATIONS

Determination	Fraction number	Weight of anhydrous chloride	Weight of silver	Ratio	Atomic weight of erbium
I	18	2.25485	2.66270	0.84683	167.69
II	19	0.30165	0.35630	,84663	167.63
III	17	1.02242	1.20761	.84665	167.64
IV	8D	0.38998	0.46068	.84654	167.60
V	8E	.38219	.45144	.84662	167.63
VI (IV)	8D	,17445	.20604	.84668	167.65
				Average	167.64

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[5] Kremers, Hopkins and Engle, THIS JOURNAL, 40, 598 (1918).

grams. The weights were standardized to 0.01 mg. and all weighings were corrected to the vacuum standard.

The following densities were used: erbium chloride, 4.1; silver, 10.5; platinum weights, 21.5; platinum plated brass weights, 8.4. The atomic weight of silver was taken as 107.88 and that of chlorine as 35.457.

Summary

1. Fractionation of erbium-yttrium material from gadolinite by the nitrate fusion method yielded erbium material of constant atomic weight, as did also fractionation of similar material by the method of fractional precipitation with sodium nitrite.

2. The ratio of erbium chloride to silver was determined in six analyses. The value 167.64 was obtained for the atomic weight as the mean of the six determinations. This value agrees with the accepted value for this element, 167.7.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

A COMPARISON OF TWO METHODS USED IN DETERMINATION OF PHOSPHORUS PENTOXIDE AS MAGNESIUM AMMONIUM PHOSPHATE

BY WALLACE MORGAN McNABB

RECEIVED AUGUST 6, 1927 PUBLISHED FEBRUARY 4, 1928

The object of this method was to check the value of the ammonium acetate method[1] in the determination of phosphorus pentoxide as magnesium ammonium phosphate with the earlier method in which ammonium acetate is not used.[2] The ammonium acetate method is designated A and the earlier method B.

In Method **A** weighed samples of monopotassium hydrogen phosphate were dissolved in 5–10 cc. of water. To this solution was added several drops of dilute 1:10 hydrochloric acid, then 25 cc. of a 20% solution of ammonium acetate and 30 cc. of magnesia mixture. (The magnesia mixture was prepared by dissolving 55 g. of crystallized magnesium chloride and 105 g. of ammonium chloride in water, adding four drops of 1:10 hydrochloric acid and diluting to a volume of 1 liter.) After heating the solution almost to boiling, several drops of phenolphthalein indicator were added drop by drop with constant stirring until a red color appeared. The solution was allowed to stand until cold ($1-1^1/_2$ hours), then about one-fifth

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[1] Schmitz, *Z. anal. Chem.*, 65, 46 (1924).

[2] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1924, vol. 2, 6th ed., p. 380.

its volume of ammonium hydroxide (sp, gr. 0.95) was added; it was stirred vigorously, allowed to stand for ten minutes and then filtered. After the precipitate was transferred from the beaker the contents of the crucible was **well** washed with *2.5%* ammonium hydroxide. The last washing was made with 4–5 drops of an ammoniacal ammonium nitrate solution (saturated); it was then dried, ignited and weighed.

In Method B the solution containing the alkali phosphate (volume **5–10** cc.) was treated with several drops of 1:10 hydrochloric acid, **30** cc. of magnesia mixture and 20 cc. of a saturated solution of ammonium chloride. After heating the mixture almost to boiling, *2.5%* ammonium hydroxide was added slowly, while constantly stirring, until a precipitate began to form, and then the addition of ammonium hydroxide was regulated so that about four drops per minute were added. As the precipitate increased, addition of ammonium hydroxide was quickened until phenolphthalein gave a red color to the solution. After cooling (1–1$^1/_2$ hours), one-fifth of the volume of strong ammonium hydroxide (sp. gr. 0.95) was added, stirred for about one minute, allowed to stand for ten minutes and then filtered. The precipitate was transferred to the crucible, washed well with 2.5% ammonium hydroxide and finally with 4–5 drops of an ammoniacal solution of ammonium nitrate (saturated), dried, ignited and weighed.

The author has found that addition of ammonium nitrate before the ignition is carried out insures formation of a pure white magnesium pyrophosphate. It aids the oxidation of any organic material present which might tend to reduce pyrophosphate in the determination of various phosphates. This procedure is especially desirable in Method A as occasionally a trace of ammonium acetate clings to the precipitate and is easily oxidized by the ammonium nitrate.

All analyses were made from definite quantities of pure recrystallized monopotassium hydrogen phosphate Each filtrate was allowed to stand for not less than twenty-four hours. Any trace of phosphate could be recognized by rubbing the bottom of the beaker with a stirring rod. This test was found to be entirely satisfactory. All filtrates gave a negative test for phosphorus. The crucible with the precipitate was placed in a porcelain crucible containing a platinum foil in the bottom.[3] The outer crucible was at first heated very gently with a Bunsen burner, the temperature being gradually increased to full red heat. The ignitions were carried out to constant weight with a Méker burner.

Since excellent results were obtained using Gooch crucibles in the determination of arsenic pentoxide as magnesium ammonium arsenate,[4] the same crucibles were used in the determination of phosphorus. With Method A the results obtained from a series of analyses using the porce-

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[3] McNabb, THIS JOURNAL, **49,891 (1927).**

[4] McNabb, *ibid.*, **49, 1451 (1927).**

lain Gooch crucible varied as much as 0.4 mg. with a 0.2000g. sample of phosphate, and there was as great a variation as 0.9 mg. for a 0.5000g. sample.

Due to these variations, the Monroe crucible was substituted. Results of the analyses are given in the table. Ignitions were carried out in the manner described above and gave a snow-white magnesium pyrophosphate. It is easier to carry out the precipitation in the presence of excess ammonium acetate. Acetate ions seem to prevent formation of secondary products and without the acetate it is tedious to produce pure magnesium ammonium phosphate. Sometimes *a* precipitate resembling aluminum hydroxide will form and is hard to filter, invariably giving high results.

Since phosphorus pentoxide is often determined as magnesium ammonium phosphate in the presence of molybdate, a check of Method A with B was made. According to Treadwell and Hall,[5] "if the solution contains more than 0.1 g. of phosphorus pentoxide, then aliquot parts for the analysis should be used." For this reason only 0.2000 g. of alkali phosphate was used for the determination of phosphorus pentoxide in the presence of molybdate ions. In analyses made by both methods and ignited to constant weight with a Méker burner, some of the ignited products retained a gray color and the results ranged from 0.1 to 0.3% high.

According to McCandless and Burton[6] "precipitates burned properly in *a* muffle do burn white and the molybdenum present is volatilized almost completely."

The table gives results of analyses using the two methods in the presence of 25 cc. of a 14% solution of ammonium molybdate, the volume of each solution being kept at 150–200 cc. Final ignitions were carried out in an electric muffle at 1000–1100° to constant weight. All ignited products on crushing were found to be white throughout. In the presence of molybdate ions a nice crystalline precipitate is easily formed using either method.

TABLE I

RESULTS OF ANALYSES

Method A

KH_2PO_4, 0.2000 g.; P_2O_5 calcd., 0.1043 g.			KH_2PO_4, 0.5000 g.; P_2O_5 calcd., 0.2609 g.		
$Mg_2P_2O_7$, g.	P_2O_5, g.	P_2O_5, diff., g.	$Mg_2P_2O_7$, g.	P_2O_5, g.	P_2O_5, diff., g.
0.1635	0.1043	0.0000	0.4097	0.2613	+0.0004
.1633	.1042	− .0001	.4090	.2609	.0000
.1637	.1044	+ .0001	.4094	.2611	+ .0002
.1636	.1044	+ .0001	.4093	.2611	+ .0002
Av. .1635	.1043	.0000	Av. .4094	.2611	+ .0002

Av. % error calcd. from 0.2000g. sample = 0.00.

Av. % error calcd. from 0.5000g. sample = +0.04.

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[5] Ref. 2, p. 382.

[6] McCandless and Burton, Ind. Eng. Chem., 19,406 (1927).

TABLE I (*Concluded*)

Method B

KH_2PO_4, 0.2000 g.; P_2O_5 calcd., **0.1043 g.**

$Mg_2P_2O_7$, g.	P_2O_5, g.	P_2O_5, diff., g.
0.1638	**0.1045**	+0.0002
.1636	.1044	+ .0001
.1631	.1040	− .0003
.1633	.1042	− .0001
.1635	.1043	.0000
Av. .1635	.1043	**.0000**

Av. % error calcd, from 0.2000g. sample = **0.00.**

KH_2PO_4, 0.5000 g.; P_2O_5 calcd., **0.2609 g.**

$Mg_2P_2O_7$, g.	P_2O_5, g.	P_2O_5, diff., g.
0.4088	**0.2608**	**−0.0001**
.4086	.2606	− .0003
.4083	.2605	− .0004
.4087	.2607	− .0002
Av. .4086	.2607	− .0002

Av. % error calcd. from 0.5000g. sample = **−0.04.**

In presence of molybdate ions

Method **A**

KH_2PO_4, 0.2000 g.; P_2O_5 calcd., **0.1043 g.**

$Mg_2P_2O_7$, g.	P_2O_5, g.	P_2O_5, diff., g.
0.1633	**0.1042**	**−0.0001**
.1635	.1043	.0000
.1634	.1042	− .0001
.1634	.1042	− .0001
Av. .1634	.1042	− .0001

Av. % error calcd. from 0.2000g. sample = **−0.05.**

Method B

KH_2PO_4, 0.2000 *g.*; P_2O_5 calcd., **0.1043 *g.***

$Mg_2P_2O_7$, g.	P_2O_5, g.	P_2O_5, diff., g.
0.1635	**0.1043**	**0.0000**
.1634	.1042	− .0001
.1634	.1042	− .0001
.1634	.1042	− .0001
.1634	.1042	− .0001
Av. .1634	.1042	− .0001

Av. % error calcd. from 0.2000g. sample = **−0.05.**

Conclusions

1. A comparison of the two methods of Schmitz in determination of phosphorus pentoxide as magnesium ammonium phosphate has been made. The ammonium acetate method is designated as Method A and the one in which ammonium acetate was not used designated as Method B. Four to five drops of an ammoniacal solution of ammonium nitrate was used in the last washing to insure complete oxidation of any organic material occasionally found in the analysis of phosphates.

2. All analyses were made from definite quantities of pure, recrystallized monopotassium hydrogen phosphate.

3. Using Method A, results obtained with porcelain Gooch crucibles and ignition carried out to constant weight with a Méker burner varied from 0.4 mg. in a 0.2000g. sample to 0.9 mg. in a 0.5000g. sample of phosphate.

4. Using Monroe crucibles and igniting to constant weight with a Méker burner, Method A gave an average percentage error of +0.02 calculated from weight of samples ranging from 0.2000 g. to 0.5000 g. Method B gave an average percentage error of —0.02.

5. In applying both methods in the presence of molybdate ions high results ranging from 0.1 to **0.3%** were obtained and some of the ignited products were of a gray color. Igniting in an electric muffle between

1000–1100° gave a white magnesium pyrophosphate. Both methods gave an average error of −0.05% (0.2000 g. sample of phosphate).

6. The advantage in Method A is that in the absence of molybdate ions it is easier to produce a crystalline precipitate.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, No. 559]

THE ACTION OF ULTRAVIOLET LIGHT ON SOME COLLOIDAL DISPERSIONS OF GOLD[1,2]

BY JACOB J. BEAVER AND RALPH H. MULLER

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Introduction

The study of the effect of radiation upon colloidal dispersions of gold has been the object of numerous investigations. The earliest of these dealt with the reducing action of light upon gold salts, with the accompanying formation of a colloidal dispersion.[3] The accelerating effect of light during the reduction of gold salts by various reducing agents has also been known for some time.[4]

A comprehensive study of the significance of light in the formation and stability of colloidal gold has been made by Nordenson.[5] His paper contains a valuable survey and criticism of previous work on this problem. He investigated the effect of light upn the reduction of chlorauric acid by hydrogen peroxide. Reduction proceeds in the darkness or diffuse daylight with the formation of a coarse, bluish suspension. The exposure to the radiation of a quartz mercury-vapor lamp, during the reduction, leads to the formation of stable sols. The degree of dispersion and the color depend upon the length of the exposure. The sols prepared in this manner were examined spectrophotometrically as well as with the ultramicroscope and the dependence of the properties upon time of exposure was demonstrated. In addition he observed a coagulating effect of the

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[1] The abstract of a thesis presented to the Graduate Faculty of Columbia University by Ralph H. Muller, October, 1925, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Presented at the September, 1926, Meeting of the American Chemical Society.

[3] (a) Hellot, "Hist. de l'Acad. de Scien.," 1737, p. 101; (b) Scheele, see Plotnikow, "Lehrbuch der Photochemie," 1920, p. 361; (c) Krüss, *Liebig's Ann. Chem.*, *43*, 237, 238, 276 (1887); (d) Rumford, Eders "Photochemie," p. 179; (e) Juch, Eders "Photochemie," p. 179; (f) Fulhame, *Ann. chim.*, **26**, 58 (1798).

[4] (a) Pelletier, *Schweigg Jour.*, 31, 317 (1800); (b) Herschel, "Hunt's Researches on Light." 1844; (c) Döbereiner, *Schweigg Jour.*, 62, *86* (1831); (d) Sonstadt, *Eders Jahrbuch f. Phot. Ind.*, 1899, *466*.

[5] Nordenson, *Inaug. Diss.*, Univ. of Upsala, 1914; *Z. physik. Chem.*, 90, 603 (1915).

ultraviolet light which is similar to that induced by weak electrolytes. He was convinced that the coagulation is not due to a photo-electric effect, because the result was the same with positively as with negatively charged particles. Some exception, however, must be taken to his method of reversing the charge on the gold particles. The method was that proposed by Burton[6] and also used by Svedberg[7] and consists in the addition of aluminum sulfate until the direction of migration under an electrical field is reversed. Nordenson admits the possibility of interaction of the gold with the products of hydrolysis of the aluminum sulfate, but apparently considers the change in sign of the particle charge to be the only important result. He could detect no chemical change in the dispersion medium which would account for the coagulation by light. He offered two explanations for the phenomenon. (1) The light may cause a difference in potential between adjacent particles (Becquerel effect) leading to attraction and eventually to precipitation, (2) The light may disturb the adsorption equilibrium between particle and associated ions, leading to instability and later to coagulation.

In attempting to reproduce some of the many photochemical phenomena ascribed to gold sols, we were impressed by the strict dependence of these effects upon the previous history of the dispersion. Thus it was possible to prepare sols which were utterly indifferent to prolonged irradiation from the most powerful artificial source of ultraviolet light available. Other sols were prepared which: by the customary mode of designation, were "clear red and free from coarse particles" and yet were markedly sensitive to ultraviolet light.

The object of this investigation is to study the conditions under which sols can be prepared which will exhibit the photochemical properties ascribed to them and to ascertain why certain dispersions are not sensitive to light and others are decidedly sensitive. In addition, the photochemical changes themselves are investigated as far as the available sources of ultraviolet light permit.

Materials Used

All solutions were made up in water having a specific conductivity of 1 to 2×10^{-6} mhos. The potassium chloride employed was recrystallized three times from conductivity water and fused in a platinum dish. The gold wire and arcing apparatus were the same as described by Beans and Eastlack[8] with the addition of an electric stirrer. C. P. nitric and hydrochloric acids were used in the preparation of the chloroauric acid.

Redistilled ether was used to prepare the solutions of phosphorus.

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[6] Burton, *Phil. Mag.*, 12, 472 (1906).

[7] Svedberg, "Die Existenz der Moleküle," Leipzig, 1912, p. 102.

[8] Beans and Eastlack, THIS JOURNAL, 37, 2667 (1915).

Forty per cent. formalin was analyzed by the method of Blank and Finkenbeiner[9] and diluted to the desired concentration with conductivity water. Thirty per cent. hydrogen peroxide (superoxol, acetanilide free) was analyzed by means of a solution of potassium permanganate, standardized against Bureau of Standards sodium oxalate. A 50% solution of hydrazine hydrate was analyzed[10] with the same permanganate solution and both reagents were diluted to the desired concentration as needed. Fused C. P. potassium carbonate was made up to tenth normal concentration. Silver nitrate solution was checked gravimetrically and by the volumetric method of Mohr. The potassium carbonate solution was standardized against a solution of hydrochloric acid which had been accurately checked against the silver nitrate solution. Pure gallotannic acid was made up to 0.1% solutions as required. Eastman hydroquinone and pyrogallol and Eimer and Amend resublimed catechol and resorcinol were employed without further purification.

Preparation of the Gold Sols

Bredig Gold Sols.—One liter of 0.0001 M potassium chloride was arced for twenty-six minutes at 3.8 amps. The solution was surrounded by an ice-bath and the arcing interrupted occasionally to prevent an undue rise in temperature. The resulting sol was centrifuged for one hour with a force equal to 1200 times gravity and then siphoned into a well steamed nonsol bottle. A few sols that had been prepared for other purposes, in hydrochloric acid, potassium iodide and potassium bromide, were also studied.

Reduction Methods.—The technique employed in making these sols was uniform with one or two exceptions. It consisted in diluting chloroauric acid, prepared from pure gold wire, to a concentration equivalent to 0.05 g. of gold per liter. A liter of this solution was carefully neutralized with 0.1 N potassium carbonate using litmus as an indicator. The reduction was carried out at 85° in a well steamed Pyrex beaker heated by an electric hot-plate. The solution was stirred rapidly by an electric stirrer and the reducing agent added at a uniform rate from a microburet. Sols were prepared with the following reducing agents: phosphorus, formaldehyde, tannin, acetylene, hydrogen peroxide, hydrazine, pyrogallol, quinol, resorcinol and catechol.

The number of reducing agents that have been used for preparing gold sols is legion. No attempt was made to exhaust all the possibilities, but rather to make a sufficient variety of sols so that the conclusions drawn from their photochemical behavior would not be restricted to a special type of dispersion.

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[9] Blank and Finkenbeiner, *Ber.*, 31, 2979 (1898).

[10] Zsigmondy, *Z. anal. Chem.*, 40, 697 (1901).

Behavior of the Dispersions toward Radiation

The gold sols, prepared as described above, were exposed to the direct radiation of a quartz mercury vapor lamp. For moderate irradiation, a 110-volt Copper-Hewitt quartz lamp was employed; while more intense light and the far ultraviolet were secured with the aid of a 220-volt Hanovia quartz lamp. Exposures were made in fused quartz flasks of about 250cc. capacity. These were thoroughly cleansed before use with aqua regia and well steamed. They were stoppered with clean new corks, care being taken that the solutions did not come in contact with the corks at any time during the experiment. The flasks were placed ten to twenty centimeters from the lamp and kept cool by a blast of air from an electric fan. This was the arrangement used for a qualitative survey of the properties of the various sols. More elaborate precautions were taken in the quantitative study of the light effects to be described later.

The preliminary experiments, made with the 220-volt lamp, showed that sols made with hydrogen peroxide, tannin, quinol, catechol, resorcinol and pyrogallol turned blue during the first two days' irradiation and then became clear red at the end of eight days' total exposure to the light. The hydrazine, phosphorus, formaldehyde, acetylene and Bredig gold sols were not affected by fourteen days' exposure to the quartz mercury arc.

These results, while only qualitative, bring out some very interesting facts, the most important being the behavior of those sols which did undergo a change in the light. They turned blue and resembled a sol to which an excess of electrolyte has been added. To use Nordenson's words, "The light has a slow coagulating effect which is very similar to that of a weak electrolyte." Unfortunately he did not observe that continued irradiation will peptize the unstable sol and produce a sol identical in appearance and behavior with the original. Since the color change evoked by electrolytes and by short exposures to light is the same, the inference, that light will completely precipitate sols, is not unnatural. However, the examination of more than a hundred gold sols prepared in a dozen different ways during the course of this investigation has shown that any colloidal dispersion of gold having associated with it the necessary stabilizing ions or possessing in general the attributes of a stable sol, though temporarily unstable for any reason, can be peptized to a stable red sol by prolonged exposure to the ultraviolet radiation from the mercury arc.[11]

In other words, any sol made blue by exposure to ultraviolet light can be restored to the original red color by prolonged exposure. Any

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[11] By stability is meant the absence of coarse particles, as indicated by strong reflection of light by the sol, or by their ready removal by the natural or augmented gravitational field. To give our criterion of stability quantitative form we may adopt the one first used by D. J. Beaver (Beaver, *Diss.*, Columbia University, 1921) which is to centrifuge the sol for one hour with a force equivalent to 1200 times gravity.

sol which is blue and unstable at the time of formation, due, let us say, to too rapid reduction, but similar in all other respects to a stable sol, can be changed to a red sol by prolonged exposure.

The effect is not due to heating of the dispersion, because in all cases the sols were kept at room temperature or lower. The peptization is not a spontaneous reaction, for it was found that dispersions that had been made blue by exposure to the light did not regain their red color for months when stored in glass bottles in the sunlight, but required about two hundred hours' exposure to the ultraviolet light to effect peptization.

After peptization is effected the light seems to have no further effect. Reasons for this will be given later.

From the qualitative data given above, one cannot draw any definite conclusions as to the reasons for photochemical sensitivity or photochemical indifference. Why, for instance, should a sol prepared with hydrogen peroxide be sensitive to light, and one prepared with formaldehyde be insensitive? It will be seen later that with the exception of the Bredig sols the conditions under which the sol is formed determine its behavior toward ultraviolet light.

The function of radiation in the formation of gold sols was not investigated in detail here because Nordenson has shown the change in color caused by different periods of exposure. An attempt was made, however, to repeat some of his experiments. The rate of formation of hydrogen peroxide sols as a function of time of exposure to ultraviolet light was followed and agreed in general with his results although the results could not be checked with the precision implied by his data. His reaction mixtures, however, were made by adding a "few drops" of hydrogen peroxide to chloro-auric acid solutions. It soon became evident that the problem had not been sufficiently investigated from the chemical standpoint and, until the effect of amount of hydrogen peroxide and other factors were known, little importance could be attached to these values.

Some of these factors were investigated for the hydrogen peroxide sols and are described later.

Behavior of Photosensitive Sols

Among those sols which had exhibited sensitivity to light in the preliminary experiments, the sols prepared by the tannin method were investigated more closely. In attempting to reproduce one of these sols, which had proved very suitable for the purpose, a sol was produced, identical in appearance, but absolutely indifferent toward radiation. It was found that slight variations in the hydrogen-ion concentration of the chloro-auric acid accounted for the differences in these tannin sols.

Electrometric titrations of the chloro-auric acid with 0.1 *N* potassium carbonate were therefore made at room temperature (22–25°). A curve was then plotted of cc. of potassium carbonate against PH of the solution for the given gold content, and from this curve solutions of definite PH were made, heated to 65° and reduced with tannin. Stirring and rate of addition of the reducing agent were uniform. The temperature was maintained to within ± 1° throughout the reduction and the time required for the appearance of the first trace of color was noted. The time values were not as reproducible as might be desired but, since so many factors are involved in the rate of reduction, this is to be expected unless unusually great precautions are taken. The values are, however, accurate enough to indicate the significance of time of reduction and its apparent relationship to the hydrogen-ion concentration and the color and stability of the dispersion.

Table I gives the results of these experiments.

TABLE I

RESULTS OF EXPERIMENTS

No.	G. of Au/liter	PH	Temp., °C.	Time of red., seconds ± 10%	Color
1	0.025	3.16	65	312	Grayish suspension
2	.025	3.43	65	217	Bluish suspension
3	.025	3.76	65	17	Purple suspension
4	.025	4.16	65	16.5	Violet sol
5	.025	4.53	65	9.3	Red sol
6	.025	4.72	65	5	Red sol
7	.025	7.66	65	14	Red sol
8	.025	8.95	65	17	Red sol, trace of blue
9	.025	9.36	65	30	Bluish-red sol
10	.025	9.63	65	58	Violet sol

It will be seen from Table I that both the color and time of reduction depend upon the hydrogen-ion concentration of the solution. The more stable red sols are formed near the neutral point and are those which are most rapidly reduced. There is a greater toleration of alkali than of acid, as it requires very high concentrations of alkali to yield a suspension. All of the unstable dispersions with the exception of the coarse suspensions (Nos. 1–3) were peptized to stable red sols by prolonged exposure to the mercury vapor lamp. The red sols (Nos. 5–8) exhibited varying sensitivity toward the light, the minimum being found, by interpolation, to be in the vicinity of PH 7.0. This supports Ostwald's statement that the most stable sols by the tannin method are those in which the chloro-auric acid is made neutral to litmus. The rather wide range (*P*H 4.53–8.95) for the clear red sols was found to be restricted to tannin, and not typical of sols prepared by other methods, and is possibly due to a protective effect of the tannin.

The influence of alkali upon the stability of gold sols prepared by the reduction method is mentioned in the literature, the statement being made that gold sols are more stable in alkaline solutions than in neutral or acid solutions.[12] Pihlblad,[13] who studied the effect of size of particle on the light absorption of disperse systems, measured the shift of the absorption band in gold sols, due to the addition of alkali to the reaction mixture. He showed a drift toward the violet, that is, the tendency to form red sols upon the addition of alkali, but did not extend his measurements far enough to show that the color passes through a clear red and then becomes blue again.

It was decided to investigate this matter more accurately, choosing the hydrogen peroxide sols as they seemed to offer less complexity than the tannin sols. The color of each dispersion was determined spectrophotometrically. For this purpose a Brace spectrometer with a variable rotating sector which could be varied while running was employed. The spectrometer table was calibrated with the following spectral lines: Li, 6708 Å.; Na, 5896, 5890 Å.; Hg(arc) 5791, 5770, 5461, 4358, 4046 Å. A large calibration chart was made from these values from which values of the wave length could be read.

The sols were made under carefully controlled conditions and were all reduced at 85°. The percentage transmission was determined for the following wave lengths: 4331, 4847, 5102, 5263, 5461, 5925 and 6549 Å. Each transmission value given is the average of several determinations. In the extreme red and violet ends of the spectrum it was necessary to take the average of three or four matchings, since the visibility maximum lies in the green and comparison in the red and violet is very difficult and fatiguing to the eye.

Table II gives the absorption data for sols reduced at different hydrogen-ion concentrations with hydrogen peroxide. Fig. 1 shows percentage transmission plotted against wave length. The last column of Table II gives the wave length corresponding to the head of the absorption band and is obtained graphically from the absorption curves.

TABLE II

ABSORPTION DATA

Sol no.	PH	Per cent. transmission for wave length of							Head of abs. band, Å.
		4331	4847	5102	5263	5461	5925	6549	
6	4.35	70.5	53.8	55.4	53.0	51.0	55.2	59.6	5510
7	6.10	49.6	39.5	35.8	33.5	34.7	52.4	77.8	5315
9	7.45	40.6	33.6	29.3	30.2	38.5	66.0	90.0	5140
25	9.40	37.4	31.2	25.9	25.6	32.1	63.4	88.1	5180
39	10.00	41.0	38.0	37.5	34.9	35.3	61.1	84.3	5345
Colorstandard		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

The Color Standard, the absorption spectrum of which is also included in Table II, is a convenient quantitative color reference and may be used

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[12] Freundlich, "Kapillarchemie," Leipzig, 1922, p. 695.

[13] Pihlblad, *Inaug. Diss.*, Univ. of Upsala, 1918.

qualitatively in judging the color of a dispersion. The standard is used by clinicians[14] and consists of 5 cc. of 20% by weight of cobaltous nitrate, $Co(NO_3)_2.6H_2O$, plus **0.30** cc. of **0.25%** of potassium dichromate solution plus 10 cc. of water.

Fig. 1 shows the progressive drift of the absorption band toward the violet end of the spectrum and then back toward the red end. Fig. **3B** shows the wave length corresponding to the maximum absorption plotted against the PH of the solution before reduction, and affords some information about the amount of colloid formed as well as its color.

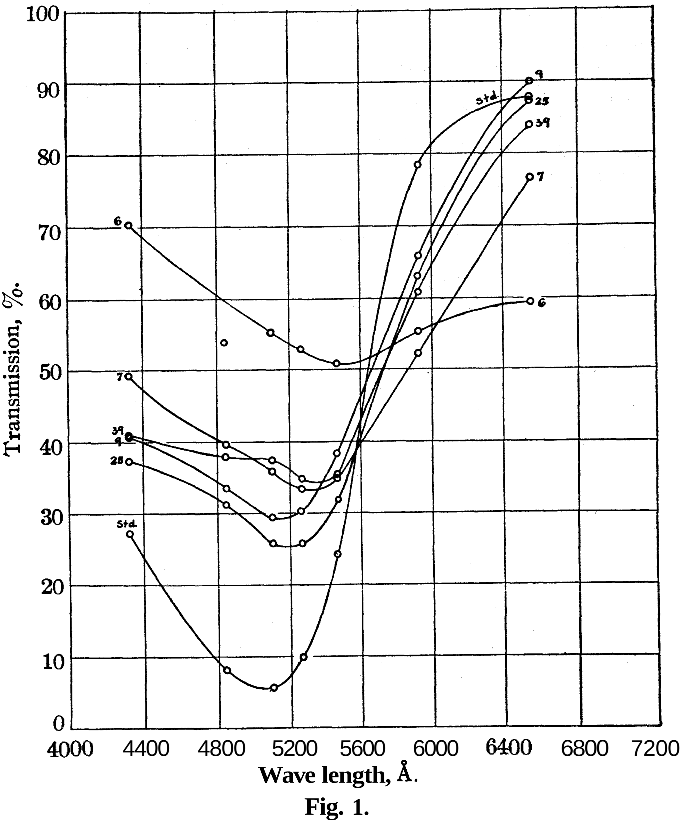

Fig. 1.

It can be seen that the transmissions at the head of the absorption bands of the bluish sols No. 6 and No. **39** are quite high, indicating little absorption of the light, while for the red sols No. 9 and No. *25* the transmissions of light at the heads of the bands are small, indicating great absorption. That this is really due to a difference in concentration of

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[14] **Wood, Vogel and Famulener, "Lab. Technique,"** St. **Luke's Hospital, New York, 1917.**

TABLE III

Concd. sol		Diluted sol (1:10)	
Wave length, Å.	Trans., %	Wave length, Å.	Trans., %
4640	19.8	4587	76.1
4950	15.7	4785	69.8
5020	12.5	4933	63.1
5100	10.0	5081	42.6
5230	7.94	5180	39.4
5270	7.94	5278	40.1
5600	10.0	5475	45.7
5750	12.5	5722	61.9
5860	15.7	5869	73.0
6060	19.8	6066	84.7
6320	24.9		

the dispersed phase was shown by mapping the absorption of a very concentrated Bredig sol and then mapping the absorption of the same

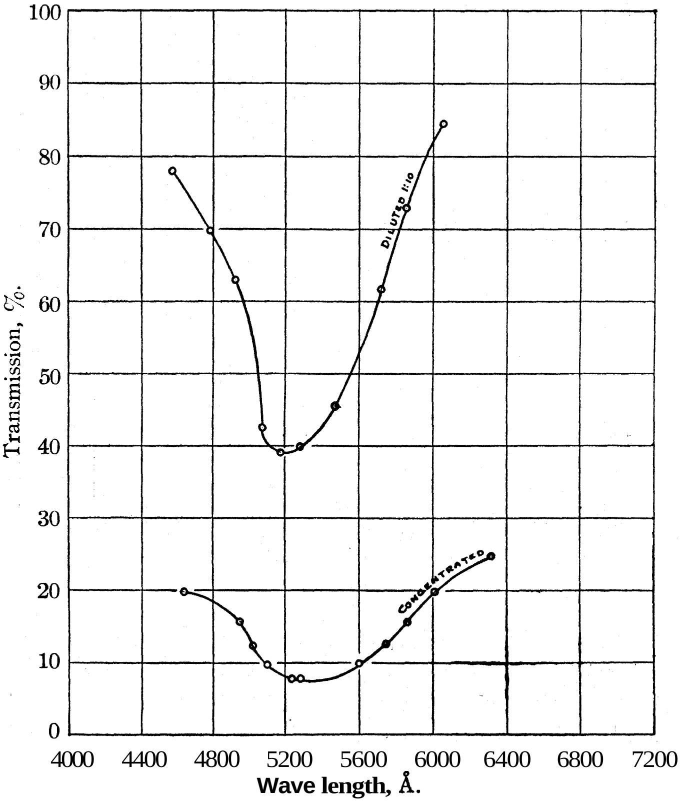

Fig. 2.

sol diluted 1:10. The maxima occur at the same wave length, but the transmissions at this wave length are 8.0 and 39.2%, respectively. The difference in shape of the curves is of little importance here, since that is influenced by reflection as well as by absorption; it is the percentage transmission at the maximum of absorption that we are concerned with. Table III and Fig. 2 illustrate this point.

Returning to the hydrogen peroxide sols, it will be seen that these experiments showed that both the color and the concentration of disperse phase are influenced by the hydrogen-ion concentration of the gold solution being reduced. This relationship is not as simple and general, however, as the above data might lead one to believe. While holding in general for the tannin sols, and quantitatively for the hydrogen peroxide sols, a similar study of dispersions made with phosphorus and hydrazine hydrate showed *a* continuous, but quite different, variation of color with hydrogen-ion concentration. Table IV gives the absorption determinations for sols prepared by the phosphorus method, and Table V the values for sols prepared by reduction with hydrazine hydrate. All reductions were carried out at 85°. The curves for these series are not plotted, as they are similar to the ones for hydrogen peroxide, but the dissimilarity is brought out by the plot of P_H against the wave length corresponding to the maximum of absorption, and is shown in Fig. **3A,** along with the one for hydrogen peroxide.

TABLE IV

PHOSPHORUS SOLS

Sol no.	P_H	Per cent. transmission for wave length of							Head of abs. band, Å.
		4331	**4847**	**5102**	**5263**	**5461**	**5925**	**6549**	
30	3.42	35.9	32.2	24.4	25.1	31.3	62.9	85.9	5110
33	4.35	44.2	33.1	24.5	23.8	26.7	59.5	84.5	5210
8	6.10	45.4	34.3	28.5	26.2	29.5	45.6	67.3	5245
3	7.45	37.2	34.5	29.5	27.1	30.0	48.1	68.4	5260
37	7.97	36.2	33.0	25.9	21.9	27.3	40.9	63.8	5270
Color standard		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

TABLE V

HYDRAZINE HYDRATE SOLS

Sol no.	P_H	Per cent. transmission for wave length of							Head of abs. band, Å.
		4331	**4847**	**5102**	**6263**	**5461**	**5925**	**6549**	
20	3.42	41.1	43.9	41.6	35.4	37.7	38.9	44.0	5300
23	4.35	32.0	38.0	37.1	33.8	33.5	40.5	53.2	5380
26	6.10	34.0	37.1	28.8	24.1	22.3	35.1	63.7	5450
29	7.97	36.3	38.3	29.0	23.0	21.7	28.8	56.3	5440
32	9.40	34.0	38.0	27.1	23.4	22.0	40.3	66.5	5410
Color standard		27.3	8.3	5.9	10.0	24.3	78.7	87.5	5040

An examination of these curves (Fig. 3) shows immediately that the phosphorus and hydrazine hydrate sols are quite different from the hydrogen peroxide sols. In the case of phosphorus sols, the optimum conditions seem to be approached in acid solutions, below P_H 4.0, and above this value are relatively uninfluenced by the hydrogen-ion concentration. The same seems to be true of the hydrazine sols, though the optimum is approached at both ends of the *P*H range. It is obvious in both cases that other factors are concerned. Chief among these is the temperature.

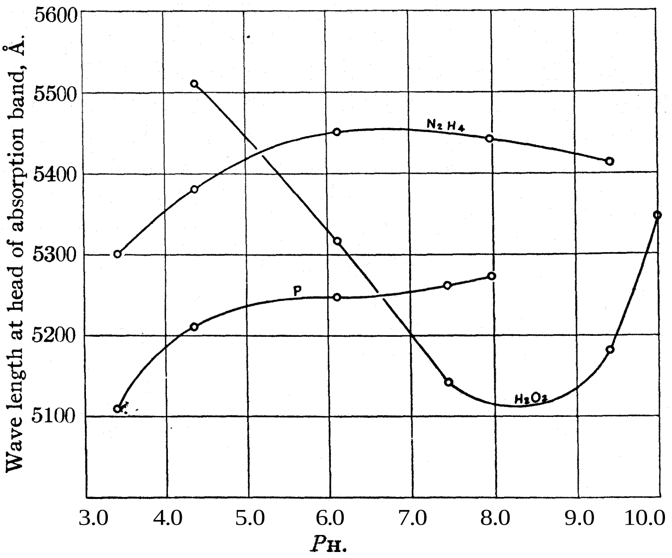

Fig. 3A.

Hydrazine sols are usually blue. At the particular temperature chosen, 85°, and over the PH range studied, they were red, with a tinge of violet. In the case of phosphorus, better sols are usually obtained by reduction

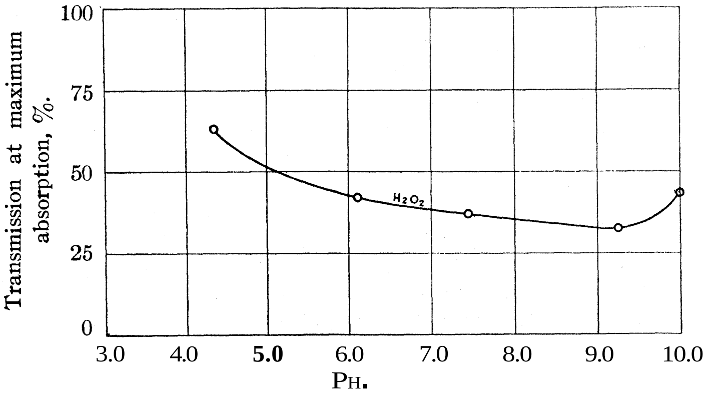

Fig. 3B.

in the cold, with subsequent heating to expel the ether. These curves show, then, that the given conditions are specific for the hydrogen peroxide sols. To establish all the criteria for stable sols of all types requires a detailed study of all the factors concerned with each specific case, and is beyond the scope of the present investigation.

Photochemically all these dispersions behaved as described above. All dispersions with a bluish or violet tinge could be peptized permanently to red sols. The sensitivity toward radiation was progressively less as neutrality was approached, and was a minimum at slight alkalinity (PH 7.5–9.0) for the peroxide sols. In this range (PH 7.5–9.0) the sensitivity, though very slight, varied, so that a number of the sols identical in appearance exhibited different behavior toward the light. All of the peroxide sols in this range would be designated as stable sols by the usual criteria of stability, so that it is evident that nothing can be predicted about the photochemical properties of a red sol from its appearance. It is only by a knowledge of the mode of preparation, such as the curve in Fig. 3 affords, that the possibility of photochemical reaction can be estimated.

The hydrogen peroxide sols were chosen for a detailed study of the photochemical properties since the general conditions for stability had been worked out and the dependence upon these conditions demonstrated. To employ red, stable sols for this purpose restricted the choice to the narrow range of hydrogen-ion concentration just mentioned, which is the range in which the light sensitivity is very small. However, it was imperative to use red sols in order to observe the various stages of the light change. The peptization of a blue sol represents only half of the phenomenon.

It soon became apparent that the most pronounced change in a sol upon illumination is the change in color. This change was followed by Nordenson in his experiments, but unfortunately it tells us little about the mechanism of the process. It is necessary to supplement such measurements with other tests in order to get an idea of the transformations taking place in the sol. With these sols the refractive index, conductivity and absorption were measured and in addition conductivity titrations were made. With the intensities of ultraviolet light at present available, these effects are very small and the utmost precision was necessary to measure them.

The reason for the small effects found was made evident by spectrograms taken in the ultraviolet with the quartz spectrograph. A fresh red sol showed complete absorption of wave lengths below 2150 Å. The same sol made blue by radiation absorbed everything below 2070 Å. and upon further exposure and peptization of this sol it absorbed all radiation below 2010 Å. If, therefore, the radiation between 2150 and 2010 Å. is responsible for the change from red to blue, it is evident that the peptized sol can undergo no further change, because it no longer absorbs the necessary wave lengths. From spectrograms taken for every sol investigated, it was found that the photosensitive sols absorbed the radiation below

2150 Å. This spectral region represents but a small fraction of the total radiant energy of the quartz mercury vapor lamp, and decreases very rapidly with the aging of the lamp. It is only with a new lamp that the far ultraviolet is available in appreciable intensity. It is for this reason that the observed effects required more than a week's exposure.

Refractive indices were determined with a Zeiss immersion refractometer, the cell containing the sol being immersed in a thermostat regulated at 25 ± 0.001°. The changes were at no time greater than five times the experimental error. A representative run was made with a somewhat more sensitive tannin sol to show the magnitude of the effect. The refractive index changed from 1.332658 in a red-violet colored sol to 1.332674 in a blue sol and then to 1.332631 in a clear red sol, which shows that there is a slight but definite increase of the refractive index as the sol becomes blue which decreases again as the sol is peptized by the radiation. Each reading of the refractive index represents the average of ten settings, and is subject to an error of eight parts in the sixth place. The hydrogen peroxide sols require about 180 hours for the same changes but the magnitude is even less. Wintgen[15] showed that in a colloidal dispersion the refractive index is a linear function of the concentration of the electrolyte and that no variation of the refractive index with degree of dispersion could be determined. Wiegner,[16] also pointed out that the linear relationship holds and could only be disturbed if varying degrees of dispersed phase affected the adsorption of ions present. In the above experiments the amount of dispersed phase is constant, so that the observed variations in refractive index would, according to these investigators, be ascribed to the substances adsorbed or otherwise associated with the colloid particle. The conductivity of the same sol under identical conditions changes in a similar manner to the extent of about 0.3%.

For an explanation of the effect of the radiation upon the sols it is necessary first of all to set forth our conception of the structure of a normal gold sol and then consider by what means radiation could modify this structure and produce the phenomena observed. Beans and Eastlack[8] have shown that anions capable of forming stable compounds with gold, in concentrations between 0.005 and 0.00005 M, are necessary for the stability of Bredig gold sols. Such ions are present in the chemically prepared sols and the two cases are probably quite similar; indeed, prolonged dialysis of any gold sol will eventually lead to precipitation.

Wilson[17] has extended the complex theory by applying the Donnan membrane equilibrium theory to it. According to him, the gold particle, combined in some manner, such as residual valence, with the stabilizing

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[15] Wintgen, *Kolloidchem. Beihefte*, 7, 266 (1915).

[16] Wiegner, *Kolloid-Z.*, **20**, 7 (1917).

[17] Wilson, THIS JOURNAL, **38**, 1982 (1916).

anion, is surrounded with a liquid layer containing cations balancing the negative charges on the particle. The distribution of ions is different in this layer than in the bulk of the solution. Consequently the Donnan membrane equilibrium theory can be applied. Though the ion concentration product is equal in the surface layer and the bulk of the solution, the concentration of anion and cation is different in the surface layer, with the surface layer having a greater total concentration than the surrounding solution. This unequal distribution of ions will give rise to a difference of potential between the enveloping film and the surrounding solution. If the concentration of ions is increased in the bulk of the solution, this difference of potential decreases and with it the stability of the dispersion.

Since no other ions enter tht solution in these experiments, it can be assumed that the radiation itself disturbs the equilibrium, causing ions to move into the bulk of the solution, thus lowering the difference of potential and consequently the stability. The solution should now be blue and have a slightly greater conductivity and refractive index, due to the presence of more ions in the bulk of the solution. But, as we have seen, the change to a blue color is accompanied by a decrease of the absorption in the ultraviolet so that the destructive effect of the radiation cannot continue without limit. A return to true equilibrium conditions then takes place with a decrease in the refractive index and conductivity and a return to the red color. The latter postulate of course implies that there are two frequencies that are effective; one which turns the sol blue and the other which turns it red. At present there is no satisfactory method of isolating narrow spectral regions of sufficient intensity to prove this point although, as in many other photochemical reactions, this is a possible explanation.

To test this hypothesis as unequivocally as possible, the largest quartz flask available was filled with a freshly prepared peroxide sol and the following properties of the sol were determined: absorption curve, conductance, refractive index. The chloride-ion concentration was also measured by means of a conductance titration with silver nitrate. All measurements were made on portions of the same sol in order to have them strictly comparable. With the particular sol employed the blue color was attained after eighteen hours' exposure and the final peptization to red again after 183 hours. Table VI gives the values of the conductivity and refractive index. Table VII gives the data for the absorption spectra, and Table VIII the data for the conductance titrations, the plots of which are shown in Fig. 4.

The values given here are to show the relationship of the values to each other for one and the same sol. Individual determinations of each property were made in number upon various sols with similar results.

TABLE VI

VALUE OF CONDUCTIVITY AND REFRACTIVE INDEX

Peroxide sol, 0.025 g. of Au/liter. $P_H = 7.45$. Reduced at 85°.

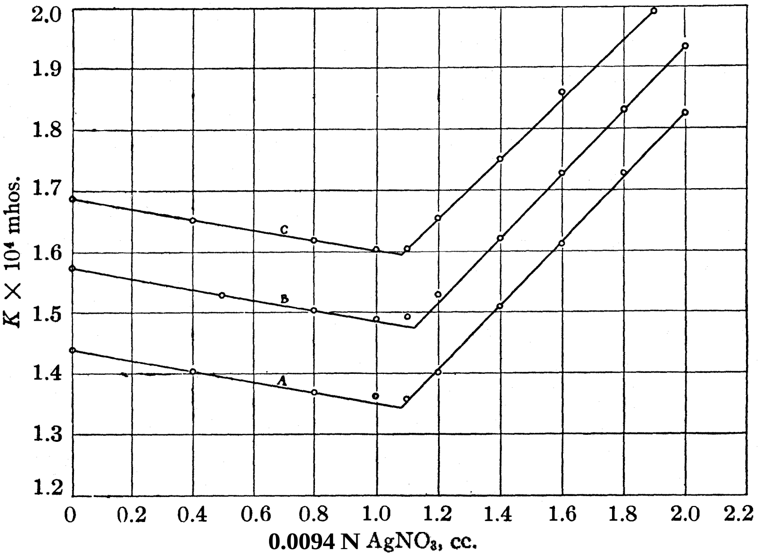
No.	Exposure, hours	Conductivity $\times 10^4$ mhos.	Refractive index, n_D	Color
2	0	1.458	1.332623	Red
2	18	1.462	1.332650	Blue
2	183	1.458	1.332623	Red

TABLE VII

ABSORPTION SPECTRA DATA

No.	Exposure. hours	Per cent. transmission for wave length of							Head of abs. band, Å.
		4331	4847	5102	5263	5461	5925	6549	
2	0	38.3	33.0	25.5	25.9	32.0	65.3	89.3	5175
2	18	49.0	43.0	35.5	31.5	33.9	52.0	69.4	5290
2	183	32.6	28.3	20.9	20.1	24.4	49.4	82.0	5210

Table VII brings out several important points. First, it will be seen that the absorption is at a maximum at 5175 Å., whereas in Table III the absorption for a sol of this P_H (7.45) is given as 5140. The difference of 35 Å., which is not a visible difference, represents the limit of reproducibility of the sols.



For curve B subtract 0.1 from value of K; for curve C, subtract 0.2.

Fig. 4.

It will also be seen that the absorption for the peptized sol (at 5210 Å.) did not quite return to the original value of 5175 Å. at the end of 183 hours, although the conductivity and refractive index had returned to the original values by that time. This emphasizes again the fact that the absorption spectrum of the dispersion is one of the most sensitive indicators of the changes taking place.

TABLE VIII

CONDUCTIVITY TITRATIONS

Sol No. 2. Titrated with 0.0094 N $AgNO_3$. Cell const. = 0.3820.

(A) Original sol		(B) After 18 hours' exposure		(C) After 183 hours' exposure	
$AgNO_3$, cc.	$K \times 10^4$ mhos.	$AgNO_3$, cc.	$K \times 10^4$ mhos.	$AgNO_3$, cc.	$K \times 10^4$ mhos.
0.00	1.439	0.00	1.474	0.00	1.487
.40	1.404	.50	1.430	.40	1.451
.80	1.370	.80	1.404	.80	1.419
1.00	1.363	1.00	1.390	1.00	1.404
1.10	1.358	1.10	1.393	1.10	1.405
1.20	1.402	1.20	1.430	1.20	1.455
1.40	1.510	1.40	1.522	1.40	1.552
1.60	1.613	1.60	1.628	1.60	1.662
1.80	1.729	1.80	1.733	1.90	1.794
2.00	1.828	2.00	1.836		

Neutral point = 1.080cc. Neutral point = 1.120 ± 0.002cc. Neutral point = 1.080cc.

These conductivity titrations indicate an increased concentration of chloride ion in the bulk of the solution in the blue sol, and a return to the original concentration in the peptized red sol. It will be observed that the initial conductivities in Table VIII do not check with those in Table VI, but are slightly higher. The samples for measurement were taken from the same solution. This discrepancy was observed on several occasions and is due to the absorption of carbon dioxide from the air. The error here is not serious for a test of the foregoing hypothesis, since it is the chloride ion with which we are concerned and its determination by the conductance titration with silver nitrate would not be influenced by the presence of dissolved carbon dioxide, due to the relatively higher solubility of silver carbonate.

The hypothesis outlined above required that the ionic concentration in the bulk of the solution should increase as the sol turns blue. The shift in color was shown and the increase in conductance as well as the greater value for the conductance titration were also demonstrated. Prolonged exposure reduced these values again and the absorption spectra showed the return to the original color.

Though the original and final red state seem to be identical, it is evident from the photochemical indifference of the latter that they are not the same. Spectrograms in the far ultraviolet bear this out, as the peptized sol no longer absorbs the effective radiation. It is possible that when peptization is effected, the ions are more firmly associated with the complex, which would account for the greater stability toward light as well as the lack of absorption bands in the effective region of the spectrum.

In addition to the above chemical sols, quantitative measurements were made on Bredig sols prepared according to the method of Beans and Eastlack.[8] Since these sols were uniformly stable to light, an attempt was made to see if their rate of precipitation by dilute solutions of electrolytes is affected by radiation.

Spear, Jones, Neave and Shlager[18] showed that the precipitation of colloidal platinum containing electrolytes is greatly accelerated by the action of ultraviolet light.

Gold sols prepared by the above method were exposed to the radiation from a quartz mercury lamp for various lengths of time and with different amounts of electrolyte (0.001 M $Th(NO_3)_4$), and the conductivity change measured very accurately. At the same time similar determinations were made on sols kept in the dark. In twenty-seven series of measurements the conductivity, which is a measure of the amount of sol precipitated, decreased at the same rate in the "illuminated" and in the "dark" sols. A plot of time divided by specific conductivity against time yielded straight lines the slopes of which depended on the amount of the electrolyte added but were independent of the kind of illumination or lack of it.

Using a photometric comparison method it was also shown that the rate of precipitation of the above Bredig gold sols was the same in the light and in the dark.

Nowhere is there a greater need for a powerful source of ultraviolet light, especially monochromatic light, than in the study of such effects as we are dealing with here. In view of the peptizing ability of the radiation as herein described, it should be possible, once such a source is available, to peptize sols during their formation or immediately after, and obtain dispersions with quite different properties.

Summary

1. The photochemical properties of gold sols depend upon the nature and method of preparation of the sols.

2. Of the sols studied, those which are sensitive to ultraviolet light are made blue and unstable by exposure, but by prolonged irradiation are peptized to stable red sols.

3. With other factors kept constant, the color, rate of formation and photochemical properties of chemically prepared gold sols were found to vary continuously with the hydrogen-ion concentration of the reduction mixture.

4. By assuming Wilson's theory of the structure of the colloidal gold particle and, further, that light can disturb the equilibria involved, it has been shown that the ion concentrations change in accordance with the requirements of the hypothesis.

[18] Spear, Jones, Neave and Shlager, THIS JOURNAL, 43, 1385 (1921).

5. The necessity for a more powerful light source for this type of investigation is emphasized.

6. The rate of precipitation of Bredig sols is not influenced by radiation.

NEW YORK CITY

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE]

THE PYROPHOSPHATE METHOD FOR THE DETERMINATION OF MAGNESIUM AND PHOSPHORIC ANHYDRIDE[1]

BY ALICE WHITSON EPPERSON

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Probably no determination in analytical chemistry has been the subject of a greater number of conflicting statements than that involving the precipitation of magnesium ammonium phosphate. It is the purpose of this paper to give the results of extensive tests of such statements, and to urge the establishment of a standard procedure which defines, so far as they are known, the most favorable conditions for obtaining a normal precipitate of $MgNH_4PO_4$, and the subsequent ignition of that precipitate to pyrophosphate, $Mg_2P_2O_7$.

In investigating the conditions most favorable for the precipitation of magnesium ammonium phosphate, methods recommended for the determination of magnesium and of phosphoric anhydride were studied. Various procedures suggested in publications on the subject since 1873 were tested, and the effects of those impurities most likely to occur in the regular course of analysis were determined. In most cases short (four hours) single precipitations were made to determine the maximum effect of any variation, and overnight (sixteen hours) single precipitations were made to determine whether standing would cause the precipitate to regain normal composition. Reprecipitation under the conditions to be recommended was tried in many cases.

Since the final treatment of the magnesium ammonium phosphate should be the same whether the precipitate is obtained in the determination of magnesium or of phosphoric anhydride, some commonly recommended methods for obtaining pure pyrophosphate were first investigated and the following observations were made. (1) Solution of the magnesium ammonium phosphate in nitric acid, followed by evaporation to dryness and igniton, has no apparent effect on the final pyrophosphate. (2) Moistening the ignited pyrophosphate with one or two drops of nitric acid, followed by re-ignition, has no effect, either good or harmful. (3) Solution of the ignited pyrophosphate in nitric acid and evaporation of the solution was found to be literally impossible, confirming the experience of Lundell and

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[1] Published by permission of the Director, National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.

Hoffman.[2] Because of decrepitation and apparent breaking down of the compound accurate results cannot be obtained.[3] None of these expedients for obtaining a white residue is desirable or necessary if care is taken in the charring of the paper and ignition of the precipitate.

Tests were also carried out to determine the concentration of ammonia solution most desirable for use as wash water for the magnesium ammonium phosphate precipitate, that having been a matter of much dispute. Many authors have recommended solutions containing one-third ammonia water by volume. Such solutions are most inconvenient to use and were found to be unnecessary and undesirable. As shown in Table I, it was found that water containing from 2.5 to 10% of ammonia water (sp. gr. 0.90) by volume could be used for washing the precipitate with equally correct results, while no advantage was found in adding ammonium nitrate to the wash water.

TABLE I

DATA OBTAINED IN TESTS OF SOLUTIONS USED FOR WASHING $MgNH_4PO_4.6H_2O$

Figures reported are averages of two or more determinations

Wash soln.[a]	Time of pptn., hrs.	Solution A = $MgCl_2$ B = $NaNH_4HPO_4$	$Mg_2P_2O_7$ equiv. of soln. taken, g.	$Mg_2P_2O_7$ found, g.	Residue after 24 hours
2.5% NH_4OH	3	A	0.0982	0.0969	In all cases residues were barely visible in filtrates from phosphate solutions; residues were visible in filtrates from $MgCl_2$ solutions but averaged less than 0.0001 *g*.
	3	B	.0953	.0953	
	24	A	.0982	.0980	
	24	B	.0953	.0956	
5% NH_4OH	3	A	.0982	.0982	
	3	B	.0953	.0955	
	24	A	.0982	.0980	
	24	B	.0953	.0954	
10% NH_4OH	3	A	.0982	.0986	
	3	B	.0953	.0952	
	24	A	.0982	.0982	
	24	B	.0953	.0951	
2.5% NH_4OH +5% NH_4NO_3	3	A	.0982	.0981	
	3	B	.0953	.0950	
	24	A	.0982	.0982	
	24	B	.0953	.0953	

[a] Wash solutions made to specified percentage by volume with ammonia (sp. gr. 0.90) and distilled water.

The procedure called "Standard Procedure" in this paper has been found by a number of operators at the Bureau of Standards to avoid the usual errors, and it is believed to afford the most favorable conditions possible for the precipitation of magnesium ammonium phosphate and its subsequent ignition to magnesium pyrophosphate. Since it is evident that

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[2] Lundell and Hoffman, *Ind. Eng. Chem.*, 15, 46 (1923).

[3] W. M. McNabb has stated [THIS JOURNAL, 49, 891 (1927)] that this treatment succeeds if the nitric acid is neutralized with ammonia before evaporation and ignition.

correct results are largely dependent on the details of the operation, the procedure given has been followed as exactly as possible in all comparative tests, except for the variations stated.

Discussion of Procedures for the Determination of Magnesium

In the determination of magnesium, microcosmic salt ($NaNH_4HPO_4$) has been most often used as the precipitant. Since it has been stated that the presence of sodium in the reagent leads to precipitates of abnormal composition and high results, various reagents were tested. It was found that slightly higher results were obtained by the use of disodium phosphate or microcosmic salt as precipitants than by the use of diammonium phosphate, $(NH_4)_2HPO_4$. This is true only of single precipitations, however, because two precipitations give practically correct results in all cases, as shown in Table II. Apparently, any abnormality or occlusion in the precipitate is remedied by reprecipitation in the presence of a slight excess of the reagent.

TABLE II

DATA OBTAINED IN COMPARISON OF PRECIPITANTS FOR MAGNESIUM AS $MgNH_4PO_4.6H_2O$

Figures reported are averages of three or more determinations

Precipitant (sat. soln.), *cc.*		No. of pptns.	Time of standing (each pptn.), hrs.	$Mg_2P_2O_7$ found, g.	$Mg_2P_2O_7 \Bumpeq MgCl_2$ taken, g.	Residue after 24 hrs.[a]
A (Na_2HPO_4)	5	1	4	0 0287	0.0280	0 0002
B ($NaNH_4HPO_4$)	5	1	4	.0285	.0280	
C $(NH_4)_2HPO_4$	3	1	4	.0280	.0280	
A	10	1	4	.0712	.0692	.0003
B	10	1	4	.0699	.0692	
C	5	1	4	.0693	.0692	
A	5	1	12	.0278	.0280	.0001
B	5	1	12	.0280	.0280	
C	3	1	12	.0280	.0280	
A	10	1	12	.0709	.0692	.0001
B	10	1	12	.0694	.0692	
C	5	1	12	.0692	.0692	
A	5	2	12	.0277	.0280	0001
B	5	2	12	.0278	.0280	
C	3	2	12	.0278	.0280	
A	10	2	12	.0691	.0692	0001
B	10	2	12	.0691	.0692	
C	5	2	12	.0691	.0692	
A	35	1	12	.6440	.6325	.0001
B	35	1	12	.6457	6325	
C	25	1	12	.6327	.6325	
A	35	2	12	.6325	.6325	.0001
B	35	2	12	.6325	.6325	
C	25	2	12	.6325	.6325	

[a] Largest residue in each series filtered after standing 24 hours, ignited and weighed.

In tests of procedures for the determination of magnesium, solutions of magnesium chloride made from Kahlbaum's c. p. salt were used. The solutions were slightly acidified with hydrochloric acid to prevent action of the alkaline solution on glass, and were kept in glass-stoppered bottles made of Jena glass. The solutions were first analyzed for magnesium content by a number of determinations as pyrophosphate. However, since this method was itself being tested, it seemed desirable to standardize the solutions by a different method. Accordingly, varying amounts of the solution, measured from a buret, were treated with precipitated mercuric oxide in water suspension. The solution was carefully dried and ignited and the process repeated until all of the magnesium chloride present was converted into oxide. It was then weighed as such. It is believed that a very accurate measure of the real magnesium content of the solution was thus obtained.[4] For the sake of convenient comparison, the weight of magnesium pyrophosphate calculated from the amount of magnesium oxide or phosphoric anhydride in the sample of solution taken is given in all tables.

Standard Procedure for the Determination of Magnesium

To the neutral or weakly acid solution of magnesium chloride, containing not more than 0.1 g. of MgO, add 5 cc. of concentrated hydrochloric acid, and methyl red indicator. Dilute the solution to 150 cc. and add 10 cc. or a 5- to 10-fold excess, of the precipitant, preferably a saturated solution of $(NH_4)_2HPO_4$. Then add ammonia water (sp. gr. 0.90) slowly, while stirring, to neutralization. Stir for about five minutes, or until the precipitate of $MgNH_4PO_4$ is well formed, then add 5 cc. excess of ammonia water and stir for ten minutes. Let stand for at least four hours, preferably overnight, filter and wash with water containing from 3 to 5% by volume of ammonia water (sp. gr. 0.90). Dissolve the precipitate by washing on the filter with warm 1:9 hydrochloric acid (sp. gr. 1.02). Add methyl red indicator and about 1 cc. of $(NH_4)_2HPO_4$ solution and finish the precipitation as before, but in a volume of 100 to 150 cc. In this precipitation digestion for four hours is sufficient. In igniting the final precipitate, the wet filter paper and precipitate should be placed in a weighed platinum crucible, charred without flaming, then ignited at a low temperature (approximately 500°) and with the lid open enough for circulation of air, until the residue is white, and finally at approximately 1000° to constant weight.

Discussion of the Results Obtained in the Determination of Magnesium

A summary of results obtained in the tests of procedures for the determination of magnesium is given in Table III. As shown in Table III-A,

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[4] Fresenius-Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, Inc., New York. 1904, Vol. 1, p. 276.

a large excess of ammonium chloride was found to produce high results for single precipitations but on reprecipitating under standard conditions the true values were obtained. Absence of ammonium chloride was found not to affect the precipitate materially.

TABLE III

DATA OBTAINED IN THE DETERMINATION OF MAGNESIUM AS $Mg_2P_2O_7$

Figures reported are averages of three or more determinations

(All precipitations as specified in standard procedure, unless otherwise specified in table. Final volume approximately 170 cc.)

Variation in standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \approx MgCl_2$ taken, g.	Wt. of $Mg_2P_2O_7$ found, g.	Remarks[a]
		III-A		
Excess NH_4Cl, *g*.				
16	1 (4 hr.)	0.1367	0.1388	(1)
16	1 (16 hr.)	.1367	.1383	(1)
16	2 (16 hr.)	.1367	.1367	(2)
None	1 (16 hr.)	.1156	.1161	(1)
1	1 (16 hr.)	.1156	.1179	(1)
5	1 (16 hr.)	.1156	.1180	(1)
10	1 (16 hr.)	.1156	.1189	(1)
25	1 (16 hr.)	.1156	.1191	(1)
		III-B		
Excess NH_4OH, cc.				
25	1 (4 hr.)	.1367	.1395	(1)
25	1 (16 hr)	.1367	.1395	(1)
25	2 (16 hr.)	.1367	.1367	(2)
40 ($^1/_4$ vol.)	1 (16 hr.)	.1367	.1366	(1)
55 ($^1/_3$ vol.)	1 (16 hr.)	.1637	.1369	(1)
85 ($^1/_2$ vol.)	1 (16 hr.)	.1367	.1397	(1)
		III-C		
Excess $(NH_4)_2HPO$				
150 cc. sat. soln.	1 (4 hr.)	.1367	.0960	(1)
	1 (16 hr.)	.1367	.1038	(1)
	2 (16 hr.)	.1367	.1370	(3) (1)
		III D		
NaCl				
0.11 g. per cc.	1 (4 hr.)	1367	.1571	Winkler procedure[5]
0.11 g. per cc.	1 (16 hr., hot)	.1384	.1427	Gibbs procedure
0.11 g. per cc.	1 (2 hr.)	.1367	.1575	Jarvinen procedure
0.11 g. per cc.	2 (16 hr.)	.1367	.1367	(2)
KCl				
0.11 g. per cc.	1 (4 hr.)	.1367	.1706	Winkler procedure
0.11 g. per cc.	1 (16 hr., hot)	.1384	.1427	Gibbs procedure
0.11 g. per cc	1 (2 hr.)	.1367	.1692	Jarvinen procedure
0.11 g. per cc.	2 (16 hr.)	.1367	.1378	3rd pptn. 0.1370

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[5] Winkler, *Z. angew. Chem.*, 32, I, 99 (1919).

TABLE III (*Concluded*)

Variation in standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \Bumpeq MgCl_2$ taken, g.	Wt. of $Mg_2P_2O_7$ found. g.	Remarks[a]
		III-E		
Pptn. made in ammoniacal soln.				
Hot soln.	1 (4 hr.)	.1367	.1405	(1)
Cold soln.	1 (2 hr.)	.1367	.1390	(1)
Cold soln.	1 (16 hr.)	.1367	.1397	(1)
Cold soln.	2 (16 hr.)	.1156	.1150	(2)
		III-F		
Jarvinen procedure	1 (2 hr.)	.1367	.1370	Pptn. in neutral soln.
		III-G		
Gibbs procedure	2 (16 hr.)	.1367	.1367	Pptn. in hot soln.
		III-H		
$(NH_4)_2C_2O_4$				
1 g. added	1 (16 hr.)	.1384	.1391	(1)
1 g. added	2 (16 hr.)	.1367	,1368	(2)
		III-K		
$(NH_4)_2SO_4$				
(5 cc. H_2SO_4, no HCl)	1 (16 hr.)	.1367	.1367	(1)
		111-I,		
Citric acid				
0.5 g. added	1 (16 hr.)	.1367	.1366	(1)
2.0 g. added	1 (16 hr.)	.1367	.1367	(1)

[a] (1) Standard procedure followed throughout except for variation noted.
(2) Reprecipitated under standard conditions.
(3) First precipitation incomplete; second precipitation made from combined precipitates recovered from the filtrate, added to first precipitate.

A large excess of ammonia was found, Table III-B, to have about the same effect as ammonium chloride. Reprecipitation, in this case also, produced a normal precipitate, with correct results. A concentration of ammonia water higher than one-third by volume was found to give high results.

As shown in Table III-C, a very large excess of the precipitant, $(NH_4)_2HPO_4$, was found to give very low results in single precipitations. Apparently, the precipitate is partially soluble in a strong solution of $(NH_4)_2HPO_4$, for further precipitation occurred when the filtrate was diluted and allowed to stand. When the complete precipitate, obtained by repeated dilution, standing and filtration, was dissolved and reprecipitated under proper conditions, the results were very nearly correct. There should be no reason, however, in the ordinary course of analysis, for the addition of such a large excess of the precipitant.

The presence of sodium chloride in the solution was found, Table III-D, to produce high results with single precipitations, but on reprecipitating true values were obtained. Equal amounts of potassium chloride gave higher and less uniform results with single precipitations than the sodium chloride. Reprecipitation under standard conditions improved the result but did not bring it within the usual limits of experimental error.

The addition of the precipitant to an ammoniacal solution has long been practiced, and even recommended. Precipitations in hot ammoniacal solution gave decidedly high results, Table III-E, as did all single precipitations in ammoniacal solutions. Reprecipitation under standard conditions of precipitates from runs made in hot ammoniacal solutions gave results which were consistently lower than the true values. Apparently reprecipitation does not remedy the error. However, there should be no reason, in the ordinary course of analysis, for the addition of the precipitant to an ammoniacal solution, since it is necessary only to acidify the solution. The danger of error in precipitations if the solution is not acid when the reagent is added, is to be emphasized.

Precipitation in a neutral solution by the method of Jarvinen[6] gave average results, Table III-F, which were only slightly high, but separate results of a series were not sufficiently uniform to be within a reasonable limit of experimental error. Since this method requires that there be no excess of ammonium salts, it would necessitate in the usual course of silicate analysis an additional time-consuming operation for evaporation to dryness and driving off ammonium salts. In the case of the presence of sodium or potassium chloride, Table III-D, the method did not lessen the error in single precipitations.

Double precipitations in hot solution, according to the method of Gibbs,[7] gave closely agreeing, true results, Table III-G. It is therefore evident that cooling the solution before precipitation is unnecessary. However, it has been found that the crystalline precipitate is formed in a slightly coarser and more easily filterable condition, with less tendency to adhere to the sides of the beaker, when precipitation is made in a cool solution. Precipitations made in hot solution in the presence of sodium or potassium chloride, Table III-D, did not seem to obviate the necessity of reprecipitating to obtain true results.

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[6] Jarvinen, Z. anal. Chem., 44, 333 (1905). In this method the solution, free from an excess of ammonium salts, is rendered neutral to lacmoid indicator and a normal solution of $(NH_4)_2HPO_4$ containing 40 cc. of 10% solution of ammonia per liter is added dropwise. When most of the precipitate has separated, a 1% solution of ammonia is added dropwise until the solution smells strongly of ammonia; then a 10% solution of ammonia to one-third the volume of the whole. The solution is filtered after two hours.

[7] Wolcott Gibbs, *Am. J. Sci.,* [3] 5, 114 (1873). Precipitation is effected with microcosmic salt from a concentrated, neutral boiling solution containing NH_4Cl. After cooling, $^1/_3$ of the volume of a 10% ammonia solution is added. No details are given as to excess of precipitant or time of standing, in which cases standard procedure was followed.

Single precipitations in the presence of ammonium oxalate gave slightly high results, Table III-H, but on reprecipitating under standard conditions correct values were obtained.

The presence of ammonium sulfate, arising from the use of sulfuric acid instead of hydrochloric in the course of analysis, showed no effect, Table III-K.

The presence of citric acid in amounts varying from 0.5 to 2.0 g. was found to have no effect on the precipitate, Table III-L.

In precipitating $MgNH_4PO_4$ from phosphate solutions containing an excess of $MgCl_2$, the results of similar variations in procedure are not always comparable to those obtained when precipitating from magnesium solutions containing an excess of phosphate.

Discussion of Procedures for the Determination of Phosphoric Anhydride

In the tests of procedures for the determination of phosphoric anhydride, solutions of diammonium phosphate, made from Kahlbaum's c. P. salt, were used. The solutions were kept in glass-stoppered Jena glass bottles and were slightly acidified with nitric acid to prevent action of the alkaline solution on the glass. The solutions were analyzed for P_2O_5 content by a number of determinations as magnesium pyrophosphate. In these determinations, a standard method, directly comparable with that used in the determination of magnesium, was used.

The only method for the determination of phosphoric anhydride which appeared practicable as a check on the magnesia method was an adaptation of the silver phosphate method. The method as used was developed for this investigation and was based on the possibility of obtaining quantitatively a uniformly normal precipitate of silver phosphate, Ag_3PO_4, the silver in which can then be obtained by the Volhard method. Various authors[8] have confirmed the value of such a method in different forms and it is believed that as given the method will be found accurate for the determination of phosphoric anhydride in solutions containing no interfering substances. The procedure developed is as follows.

To the cool phosphate solution, very slightly acid with nitric acid, and containing not more than 0.1 g. of P_2O_5, add 5 cc. of a saturated solution of sodium acetate. Add an excess of 10% silver nitrate solution until no more precipitate appears. Heat on the steam-bath for about ten minutes, then filter through a Gooch crucible and wash thoroughly with hot water. Dissolve the precipitate by washing through the crucible with dilute nitric acid (1:4, sp. gr. 1.10) and titrate with a standard solution of potassium thiocyanate, by the Volhard method, using ferric ammonium sulfate as

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[8] (a) Kolthoff, *Pharm. Weekblad*, 59, 205 (1922); (b) Clark, *J. Soc. Chem. Ind.*, 7, 311 (1888); (c) Holleman, *Z. anal. Chem.*, 33, 185 (1894); (d) Wilkie, *J. Soc. Chem. Ind.*, 29, 794 (1910).

indicator. Comparative results showing the degree of uniformity and the very close agreement between this and the pyrophosphate method, are given in Table IV.

TABLE IV

DETERMINATION OF PHOSPHORIC ANHYDRIDE

Solution	Grams per cc.[a] P_2O_5 (weighed as $Mg_2P_2O_7$)	P_2O_5 (titrated as Ag_3PO_4)
$NaNH_4HPO_4$	0.00682	0.00686
$(NH_4)_2HPO_4$	.01045	.01045
$(NH_4)_2HPO_4$	.00930	.00930
$(NH_4)_2HPO_4$	.00956	.00956

[a] Each result is the average of at least three closely agreeing determinations

Standard Procedure for the Determination of Phosphoric Anhydride

To the neutral or weakly acid solution of phosphate, containing not more than 0.1 g. of P_2O_5, add 5 cc. of concentrated hydrochloric acid, and methyl red indicator. Dilute the solution to 150 cc. and add 10 cc. or a 5- to 10-fold excess, of the precipitant, preferably magnesia mixture without ammonia (50 g. of $MgCl_2.6H_2O$, 100 g. of NH_4Cl and 5 cc. of concentrated HCl in 1 liter of H_2O). The solution should be acid after the addition of the precipitant. Then add ammonia water (sp. gr. 0.90) slowly, while stirring, to neutralization. Stir for about five minutes, or until the precipitate of magnesium ammonium phosphate is well formed, then add 5 cc. excess of ammonia water and stir for ten minutes. Let stand for at least four hours, preferably overnight, filter and wash with water containing from 3 to 5% by volume of ammonia water (sp. gr. 0.90). Dissolve the precipitate by washing on the filter with warm 1:9 hydrochloric acid (sp. gr. 1.02). Add methyl red indicator, 1 cc. of magnesia mixture and finish the precipitation as before but in a volume of 100 to 150 cc. In this precipitation digestion for four hours is sufficient. In igniting the precipitate, the wet filter paper with the precipitate should be placed in a weighed platinum crucible, charred without flaming, then ignited at a low temperature (approximately 500°) and with the lid open enough for circulation of air until the residue is white, and finally at approximately 1000° to constant weight.

Discussion of the Results Obtained in the Determination of Phosphoric Anhydride

As shown by figures given in Table V-A, an excess of ammonium chloride was found to give high results in single precipitations as in the case of magnesium. When the solutions were allowed to stand for sixteen hours the results, however, were better. On reprecipitating under "standard" conditions, the results were correct. Absence of added ammonium chloride did not affect the precipitate materially. It will be noted that in the case of large excess of ammonium chloride (25 g.) results were low, differing from the determination of magnesium. Apparently the same effect is noted later (Table V-C) where it is indicated that the presence of ammonium chloride has a tendency to compensate for high results due to large excess of magnesium chloride.

TABLE V

DATA OBTAINED IN DETERMINATION OF PHOSPHORIC ANHYDRIDE AS $Mg_2P_2O_7$

Figures reported are averages of three or more determinations

(All precipitations as specified in standard procedure, unless otherwise specified in table. Final volume approximately 170 cc.)

Variation from standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \approx P_2O_5$ taken, g.	Wt. of $Mg_2P_2O_7$ found, g.	Remarks[a]
		V-A		
Excess NH_4Cl, g.				
16	1 (4 hr.)	0.1458	0.1463	(1)
16	1 (16 hr.)	.1458	.1461	(1)
16	2 (16 hr.)	.1458	.1457	(2)
None	1 (16 hr.)	.1496	.1499	Results not uniform
1	1 (16 hr.)	.1496	.1500	Results not uniform
5	1 (16 hr.)	.1496	.1500	Results not uniform
10	1 (16 hr.)	.1496	.1499	(1)
25	1 (16 hr.)	.1496	.1473	(1)
		V-B		
Excess NH_4OH, cc.				
25	1 (4 hr.)	.1458	.1473	(1)
25	1 (16 hr.)	.1458	.1459	(1)
25	2 (16 hr.)	.1458	.1457	(2)
40 ($^1/_4$ vol.)	1 (16 hr.)	.1458	.1458	(1)
55 ($^1/_3$ vol.)	1 (16 hr.)	.1458	.1465	(1)
85 ($^1/_2$ vol.)	1 (16 hr.)	.1458	.1473	(1)
		V-C		
Excess Mg mixture, cc.				
100	1 (4 hr.)	.1458	.1520	(1)
100	1 (16 hr.)	.1458	.1487	(1)
100	2 (16 hr.)	.1458	.1457	(2)
150	1 (10 min.)	.1458	.1445	Schmitz method
100 cc. Mg mix.				
14 g. NH_4Cl added	1 (16 hr.)	.1458	.1485	Mahon method
25 g. NH_4Cl added	1 (16 hr.)	.1458	.1480	Mahon method
2 g. NH_4Cl added	1 (16 hr.)	.1458	.1430	Mahon method
No NH_4Cl added	1 (16 hr.)	.1458	.1216	Mahon method
		V-D		
Pptn. made in ammoniacal soln.				
4 cc. NH_4OH	1 (3 hr.)	.1458	.1462	Neubauer
(2.5% by vol.)	2 (16 hr.)	.1458	.1468	Neubauer
(2.5% by vol.)	2 (16 hr.)	.1496	.1505	(1) (2)

TABLE V (*Concluded*)

Variation from standard procedure	No. of pptns.	Wt. of $Mg_2P_2O_7 \approx P_2O_5$ taken, g.	Wt. of $Mg_2P_2O_7$ found. g.	Remarks[a]
		V-E		
Jarvinen procedure	1 (2 hr.)	.1458	.1464	Neutral soln.
		V-F		
Pptn. made in hot soln.	1 (16 hr.)	.1458	.1460	In comparison with Gibbs' method for Mg (1) (2)
	2 (16 hr.)	.1458	.1463	
		V-G		
$(NH_4)_2SO_4$ present	1 (16 hr.)	.1496	.1520	H_2SO_4 substituted for HCl in standard procedure (2)
$(NH_4)_2SO_4$ present	2 (16 hr.)	.1496	.1502	
		V-H		
Citric acid, g.				
2	1 (16 hr.)	.1458	.1443	(1)
0.5	1 (16 hr.)	.1458	.1450	
0.5	2 (16 hr.)	.1458	.1451	(1) (2)

[a] (1) Standard procedure followed except for variation noted.
(2) Reprecipitated under standard conditions.

Excess ammonium hydroxide was found, Table V-B, to have substantially the same effect as in the determination of magnesium. A concentration higher than $^1/_4$ volume was found to give high results, as in the determination of magnesium, while reprecipitation gave correct results.

A large excess of the precipitant ($MgCl_2.NH_4Cl$) was found, Table V-C, to give high results on single precipitation, correct results being obtained by reprecipitating under standard conditions. Precipitations by the method of Schmitz[9] gave low results, probably owing to the extremely short time allowed before filtering. Tests of Mahon's assertion[10] that excess of ammonium chloride compensates for the error due to excess of magnesia mixture, showed his statements to be incorrect. However, results were very low when no ammonium chloride, or very small amounts, were present, indicating that the presence of this salt has the tendency claimed, but does not wholly remedy the condition.

Precipitations made in ammoniacal solutions were found, Table V-D,

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[9] Schmitz, Z. anal. Chem., **45, 512 (1906);** *ibid.,* **65, 46 (1924).** A large excess (**150** cc.) of acidified magnesia mixture and **10–20** cc. of a saturated solution of NH_4Cl are added, the solution is heated to boiling and a **2.5%** solution of ammonia added, with constant stirring, until the solution is alkaline to phenolphthalein. The solution is then cooled and one-fifth of its volume of ammonia is added. The solution is filtered after standing for ten minutes.

[10] Mahon, THIS JOURNAL, 20, **445 (1898).** The method is not described in detail. It is stated that when $MgCl_2$ is in large excess the error is reduced by the presence of NH_4Cl, but the ratio necessary for accurate results is not indicated.

to give high results, contrary to statements of Neubauer.[11] Reprecipitation under standard conditions did not remedy the error.

Precipitations in exactly neutral solution, according to the method of Jarvinen,[12] gave results, Table V-E, that were not uniform and averaged slightly higher than the true figure, as was the case in the determination of magnesium.

Precipitations in hot solution gave slightly high results, Table V-P, differing from the determination of magnesium, which was not affected by the temperature of precipitation.

The presence of ammonium sulfate, owing to the use of sulfuric acid instead of hydrochloric, gave high results, Table V-G. In the determination of magnesium it had no effect.

Precipitations in the presence of citric acid, Table V-H, gave low results which were not uniform. This was not entirely remedied by reprecipitation under standard conditions.

Conclusions

The most significant fact brought out by these studies is that a double precipitation, the second under exactly defined conditions, is necessary, to insure the quantitative precipitation of $MgNH_4PO_4$. Consequently this procedure should be followed in all accurate work. It is also demonstrated that in the determination of magnesium the errors due to (1) a very large excess of precipitant, (2) the presence of potassium chloride and (3) the addition of the precipitant to an ammoniacal solution, were not entirely remedied by reprecipitation. These conditions may easily be avoided, however, except that due to excess of potassium chloride. In this case it was found that a third precipitation usually gave a precipitate of the desired composition and a correct result.

In the determination of phosphoric anhydride the only errors not remedied by reprecipitation are those due to (1) addition of the precipitant to the solution while ammoniacal, (2) precipitation in hot solution (slight

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[11] Neubauer, *Z. anorg. Chem.*, 4, 251 (1893); *Z. angew. Chem.*, 9, 435 (1896). The phosphate is precipitated in 100 cc. of a cold solution containing 2.5% of ammonia by adding dropwise, with constant stirring, as many cc. of magnesia mixture as there are centigrams of P_2O_5 present. The solution is then stirred, allowed to stand for three hours, filtered, the precipitate washed with a 2.5% solution of ammonia and ignited to constant weight. A correction for loss on ignition is added by the author.

[12] Jarvinen, *Z. anal. Chem.*, 43, 279 (1904). The phosphate solution is mixed with NH_4OH until the odor of ammonia is noted. The solution is poured slowly, with constant stirring, into a neutral mixture of $MgCl_2$ and NH_4Cl. Free ammonia should be absorbed by the formation of the precipitate. If the mixture smells of ammonia, trimagnesium phosphate may be formed. After precipitation is complete, a 0.5% solution of ammonia is added until a strong odor of ammonia is detected; finally, one-third of the volume of a 10% solution of ammonia. The mixture is allowed to stand for two hours and filtered.

error only), (3) the presence of ammonium sulfate and (4) the presence of citric acid. The first two can be avoided; while the error caused by sulfate is negligible in any but the most accurate work.

The general impression of great difficulty and inaccuracy that has surrounded the determination of magnesium and phosphoric anhydride as magnesium pyrophosphate, is largely the effect of the mass of conflicting publications on the subject. The standard procedures here recommended have been found to give accurate results with reasonable care and the data presented should answer many questions as to the value of recommendations to be found in the literature on the subject.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

THE EQUILIBRIUM PRESSURE OVER COEXISTING SALT HYDRATES AT TEMPERATURES BELOW 0°

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The phase relations for salt hydrates have been worked out fairly completely but there remain one or two minor points which appear not to have been specifically discussed. One of these is the question as to whether the vapor pressure curve of a system composed of two adjacent hydrates and vapor intersects the ice-vapor curve in the low temperature region.

The principle involved will be evident from a consideration of the P-T diagram as given in Fig. I. The hydrates are denoted by S_1, S_2, S_3, etc.; the saturated solution by L, other solutions by L^{I}, L^{II}, etc.; ice by I and the vapor by V. The vapor pressure of all unsaturated solutions of the salt ranges between the water line and the line representing the vapor pressure of the system S_1-L-V; that of the system S_1-S_2-V is another line below the S_1-L-V line. Similarly, if other hydrates exist, there is a corresponding curve, for example, S_2-S_3-V for each pair of adjacent hydrates. Now the line for the unsaturated solution intersects the ice curve at the ordinary freezing temperature of the particular solution, the phases then present being I-L^{I}-V; that for the saturated solution S_1-L-V intersects the ice curve at the eutectic temperature, the four coëxisting phases being S_1-I-L-V. The question now arises as to whether the curve for systems composed of two hydrates and vapor will meet the ice-vapor curve if the temperature is sufficiently low; this point must, according to Blasdale, be considered.[1] Such an intersection would imply

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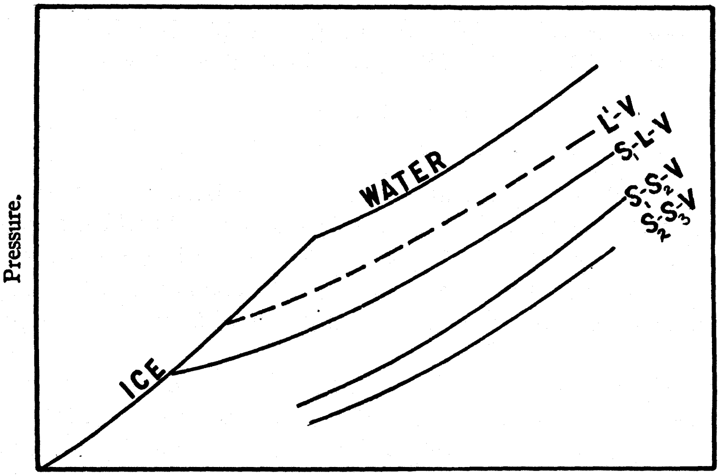
[1] Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Company, New York, 1927, p. 39.

a curious non-variant point at which I-S_1-S_2-V would be in equilibrium; or, in other words, that on cooling the system to a low enough temperature, solid water should split out from the higher hydrate provided the rate of reaction is appreciable. It is the purpose of this paper to consider such data as are available in order to ascertain the course of the vapor pressure curve for this type of system at low temperature.

From general theoretical considerations alone, the reality of such a point seems doubtful. In order that a hydrate may form, the tendency of the H_2O molecules to unite with the salt or salt hydrate molecule must be greater than the tendency to unite with one another. Hence, it seems likely that the escaping tendency of the H_2O molecules from a hydrate will always be less than from ice or, in other words, the vapor pressure curve of the hydrate pair system must always be below the ice-vapor curve.



Temperature.

Fig. 1.—The equilibrium pressure over coexisting salt hydrates below 0 °C.

Furthermore, Norton and Johnston[2] have shown that the equilibrium pressure over two adjacent hydrates may be determined by adding to a solution in equilibrium with both solid hydrates, a third soluble component, and then measuring the vapor pressure at the new transition temperature, which by regulation of the added solute can be made to have a range of values. Under such circumstances the vapor pressure of this system is equal to the equilibrium pressure of the two crystalline hydrates at the particular temperature, provided always that both hydrates are present as solid phases. Hence, if the hydrate curve is to cut the ice curve, the vapor pressure of the system S_1-S_2-L''-V (where L'' is the equilibrium solution containing also the third component) must at some

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[2] Norton and Johnston, Am. *J. Sci.*, 12, 467 (1926).

temperature be equal to that of the system I-L''-V, a coincidence which would appear to be exceedingly improbable as a general rule.

The experimental data available are in accord with these conclusions. Vapor pressures plotted on a P-T diagram are not satisfactory for this purpose because data at low temperatures are not always available and extrapolation with any certainty is impossible. The plot of log p versus $1/T$ is no better because in some cases the lines are so nearly parallel to the ice-vapor curve that again uncertainty exists. But this log plot may be used in another way. The lines on this plot may be represented by the equation

$$\log p = \frac{Q}{2.3RT} + B$$

where p is the vapor pressure of the system, Q is the heat effect, T is the absolute temperature and B is a constant, so that their slope is proportional to the quantity Q. Now Q is the sum of several factors; for ice these are the heat of fusion of ice and the heat of vaporization per mole of water; for the hydrate, the heat of hydration plus the heat of vaporization per mole of water. The heat of vaporization of water appears in both so that any difference in Q is due to a difference between the heat of fusion of ice and the heat of hydration of the salt (or salt hydrate) per mole of water. It is obvious that if the heat of hydration of the salt per mole of water is greater than the molal heat of fusion of ice, the curves will not intersect and that they will intersect only if the converse holds.

The heats of hydration per mole of water have been calculated from the tables of Landolt-Börnstein[3] for some 200 salt hydrates and of this number only 10 showed a value of less than 1.437 cal., the molal heat of fusion of ice.[4] About 70% of such values were between 2.0 and 4.0, the average for all being **3.6.** These heat effects are not given for the temperatures under discussion but they are in general so much greater than 1.4 that it seems unlikely that their relative values will be altered very much by lowering the temperature.

The ten exceptions are: $KSH.{}^1/_4H_2O$, $K_2SO_3.H_2O$, $K_2S_2O_3.H_2O$, $KC_5H_7O_4.H20$ (pyrotartrate), $KC_4H_5O_5.H_2O$ (malate), $KC_4H_5O_4.H_2O$ (methyl malonate), $K(SbO)C_4H_4O_6.{}^1/_2H_2O$, $NaC_4H_7O_2.3H_2O$ (butyrate), $NaC_5H_9O_2.1{}^1/_2H_2O$ (valerate), $Sr(C_2H_3O_2)_2.{}^1/_2H_2O$.

A critical examination of the original sources shows that these ten values are open to criticism and suspicion. In the case of $KSH.{}^1/_4H_2O$, Sabatier's method[5] of preparation has since been shown to yield a product different from the above. The remaining values are due to Berthelot,[6]

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[3] Landolt-Börnstein-Roth-Scheel, "Physikalish-ChemischeTabellen," 5th Edition, 1923, p. 1570.

[4] Dickinson and Osborne, *Bull. Bur. of Stand.*, **12,** 49 **(1915).**

[5] Sabatier, **Ann.** *chim. phys.*, [5] 22, **21 (1881).**

[6] Berthelot, "Thermochemie," Gautier Villars and Sons, Paris, 1897, Vol. II.

Massol[7] and Guntz.[8] The data of Berthelot were taken before he developed his bomb calorimeter and are obtained by difference from other measurements at different temperatures. Furthermore, his calculations are based on O = 8. Massol's work and the paper by Guntz come under these last objections; moreover, in no case are there data from which the degree of purity of the materials used may be estimated. In addition, the paper by Guntz contains a number of obvious typographical errors which tend to lessen confidence in his results.

In view of the striking agreement in all cases except those in which the data seem not to be reliable, it may be safely concluded that the two vapor pressure curves do not intersect and that this non-variant point does not in fact exist. From this it follows that under all conditions the vapor pressure of water above a pair of adjacent hydrates is less than that above ice or water. This means that the heat of hydration of salts per mole of water must always be less than the molal heat of fusion of ice, which furnishes a valuable criterion for the critical examination of experimental data on vapor pressures of salt hydrate pairs and on heats of hydration.

The author wishes to acknowledge his indebtedness to Dr. J. Johnston and Prof. H. W. Foote, whose criticism and advice have been most helpful.

Summary

It is shown that at any temperature the vapor pressure of water over a system composed of two solid hydrates and vapor must always be less than the vapor pressure of ice. This furnishes a criterion of the accuracy of data on the heats of hydration of salts.

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[7] Massol, *Ann. chim. phys.*, [7] 1, 145 (1894).

[8] Guntz, *ibid.*, [6] 13, 388 (1888).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

OXIDATION OF HYDRAZINE
VIII. MONO-BELECTRONATORS AND DI-DELECTRONATORS[1]

BY R. E. KIRK AND A. W. BROWNE

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Among the objectives of the current series of investigations have been (1) an elucidation of the mechanism involved in the oxidation of hydrazine and (2) a general classification of oxidizing agents,[2] possibly valid also in other reactions.

When the attempt is made to group oxidants together on the basis of their behavior toward hydrazine, it is found that substances of widely divergent oxidation potentials fall into the same category. It has been shown by extended experiments that the peroxide, permanganate and manganic ions, all of high potential, give distinctly different results when brought into contact, under similar conditions, with hydrazine ions in the presence of sulfuric acid. Hydrogen peroxide yields large amounts of both hydronitric acid and ammonia;[1a,1d,1f] potassium permanganate, small amounts of hydronitric acid and large amounts of ammonia;[1d] and manganic acetate no hydronitric acid but large amounts of ammonia.[3] On the other hand, the arsenate ion yields hydronitric acid and ammonia,'' while the cupric ion, of similar potential, gives ammonia but no hydronitric acid.[1e]

On the basis of these facts, hydrogen peroxide and arsenic acid would be grouped together, despite the marked disparity in their oxidizing power. Similarly, manganic and cupric salts would be placed in the same class. These instances are fairly typical of the large number that might be adduced.[4]

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[1] For the earlier articles of this series see (a) Browne, THIS JOURNAL, 27,551 (1905); (b) Browne and Shetterly, *ibid.*, 29, 1305 (1907); (c) 30, 53 (1908); (d) 31,221 (1909); (e) 31, 783 (1909); (f) Hale and Redfield, 33, 1353 (1911); (g) Hale and Nunez, 33, 1555 (1911); (h) Browne and Overman, 38, 285 (1916). The present work is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by R. E. Kirk, Grasselli Fellow in Chemistry, 1926–1927, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

This article is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as Article No. 6 in the Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University.

[2] Ref. 1 e, p. 797.

[3] Bray and Cuy, THIS JOURNAL, 46, 1796 (1924).

[4] Against the possible vague contention that this anomalous collocation of dissimilar oxidants might be attributed to specific catalytic effects may be cited the fact that both positive and negative ions are included in each of the groups concerned. It would be difficult to conceive of a catalytic process sufficiently broad in its scope to cover all of the cases under consideration.

Oxidation and Reduction as Delectronation and Electronation

It was stated in 1903 by J. J. Thomson[5] that: "A univalent electro-positive atom is one which under the circumstances prevailing when combination is taking place, has to lose one and only one corpuscle, before stability is attained; a univalent electro-negative atom is one which can receive one, but not more than one, corpuscle without driving off other corpuscles from the atom; a divalent electro-positive atom is one that loses two corpuscles and no more, and so on."

In the same year, Abegg[6] expressed more definitely the ideas first pre-adumbrated by Berzelius,[7] and later outlined by Ostwald,[8] concerning the relationship between chemical action and electric charges. The close correspondence now recognized between chemical and electrochemical actions is a logical outgrowth also of the epochal discoveries of Faraday.[9] According to Bancroft,[10] "The most striking characteristic of an electrolytic reaction is that it occurs in two places—at the anode and at the cathode. The peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes, we have a chemical reaction in the ordinary sense of the word, and not an electrochemical reaction."

The view that oxidation and reduction involve a transfer of electrons has been widely disseminated by Alexander Smith[11] and by Stieglitz,[12] who also extended the idea to the oxidation of organic substances. Similar concepts have been employed by Falk and Nelson,[13] by Fry,[14] and by L. W. Jones[15] and their associates to explain organic reactions.

The reasons for considering the fundamental mechanism in reactions of oxidation and reduction to involve a transfer of electrons have been carefully reviewed by Cady and Taft,[16] who believe that "in the absence of any proof to the contrary, the most convenient and the most generally

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[5] Thomson, Silliman Lectures at Yale University, published under title "Electricity and Matter," Scribners, New York, 1905.

[6] Abegg, *Z. physik. Chem.*, 43,385 (1903); *Z. anorg. Chem.*, 39,330 (1903).

[7] Berzelius, "Lehrbuch der Chemie," Erster Band, Arnold'sche Buchhandlung, Dresden and Leipzig, 1843, p. 105, 110.

[8] Ostwald, "The Scientific Foundations of Analytical Chemistry," 1st ed., trans. by McGowan, Macmillan Company, New York, 1895, pp. 90–98.

[9] Faraday, "Experimental Researches," Vol. I, Series III, $8, p. 102; Series VII, $11, p. 1195.

[10] Bancroft, *Trans. Am. Electrochem. Soc.*, 8, 33 (1905); 9, 13 (1906).

[11] Smith, "General Chemistry for Colleges," The Century Co., New York, 1916, p. 322.

[12] Stieglitz, "Qualitative Chemical Analysis," The Century Co., New York, 1911.

[13] Falk and Nelson, THIS JOURNAL, 37, 1732 (1915).

[14] Fry, ibid., 37, 2368 (1915).

[15] L. W. Jones, ibid., 39,674 (1917).

[16] Cady and Taft, *J. Phys. Chem.*, 29,1057,1075 (1925).

correct view is to regard the process as a direct transfer of charges. . ., a conception which is also in accord with the present electronic theory of valence. It must be understood that we are advancing no arguments against the formation of intermediate compounds in oxidation and reduction reactions, as there is experimental evidence on record in so large a number of cases that this is not a question for argument."

Direct evidence of reduction effected by electrons supplied either from a spark cathode or by the β-radiation from radium, and of oxidation effected by a-particles from radium has been presented by Pisarzhevskii and Rosenberg.[17] The restoration of electrostatic equilibrium through certain membranes that show ionic selectivity has been demonstrated by Girard and Platard[18] to occur as the result of a transfer of electrons rather than of ions.

On the basis of such experimental evidence as the foregoing, it seems reasonable to conclude that oxidation is to be regarded as essentially a process of *delectronation*,[19] and reduction as electronation.

Mono-Delectronators and Di-Delectronators

Oxidizing agents may be grouped in two classes: (1) those that accept one electron only per active unit (atom, ion or molecule) and *(2)* those able to accept more than one electron per active unit. Members of the first class, including such oxidants as ferric, manganic, ceric and cupric ions, may be termed mono-delectronators. The second class comprises *di-delectronators*[20] such as peroxide, chlorate and persulfate ions, as well as possible *tri-delectronators* and other *poly-delectronators*.[21]

Oxidation of Hydrazine by Mono-delectronators.—Hydrazine may be completely oxidized, under appropriate conditions, to nitrogen and water. Whenever its oxidation by mono-delectronators is incomplete, the sole by-product formed is ammonia. This may be most readily explained by assuming initial liberation of univalent N_2H_3 residues, or free radicals, each of which contains an atom of bivalent nitrogen, in accordance with the equation

$$N_2H_5^+ - \ominus = N_2H_3 + 2H^+ \qquad (1)$$

Subsequent condensation of two such residues would yield tetrazane, $NH_2.NH.NH.NH_2$, a compound of which organic derivatives have long

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[17] Pisarzhevskii and Rosenberg, *J. Russ. Phys.-Chem. Soc.*, *54*, 533, *548*, 570 (1923); C. *A.*, 18, 1424,2835 (1924).

[18] Girard and Platard, *Compt. rend. soc. biol.*, 90,932,933, 1020 (1924).

[19] "Delectronation" seems to the authors more euphonious than "de-electronation," which has been proposed by Cady and Taft [*Science*, 62,403 (1925)].

[20] "Mono-delectronator" and "di-delectronator" were first suggested in this Laboratory by E. W. Phelan in place of the rather cumbersome terms one-equivalent oxidizing agent and two-equivalent oxidizing agent.

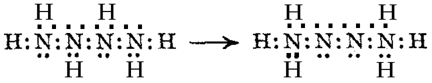
[21] A similar classification of reducing agents as *mon-electronators*, *di-electronators*, and *poly-electronators* is also possible.

been known.[22] Decomposition of this intermediate product would undoubtedly take place with formation of ammonia and nitrogen:

$$N_4H_6 = N_2 + 2NH_3 \qquad (2)$$

The first of these stages, that of delectronation, must be a reaction of the second order, as demonstrated by Bray and Cuy,[3,23] for the oxidation of hydrazine by the typical mono-delectronators, manganic ion and ferric ion. The second and third stages must proceed with greater velocity than the first, as otherwise further delectronation of the residues, either before or after condensation, would be evidenced.

Decomposition of the tetrazane may be conceived to involve a simple migration of two hydrogen nuclei, presumably very mobile, from the central to the external nitrogen atoms of the chain, in accordance with the conventional electronic diagram



$$H:\overset{H}{\underset{\cdot\cdot}{N}}:\underset{H}{N}:\overset{H}{\underset{\cdot\cdot}{N}}:\underset{H}{N}:H \longrightarrow H:\overset{H}{\underset{H}{N}}:\underset{\cdot\cdot}{N}:\underset{\cdot\cdot}{N}:\overset{H}{\underset{H}{N}}:H$$

with ultimate formation of a labile compound of molecular nitrogen and ammonia, $N_2.2NH_3$.

Among the mono-delectronators previously studied in this Laboratory'' are ferric, cupric, nickelic and cobaltic ions. Each of these oxidizes hydrazine under the specified conditions with formation of water, nitrogen and ammonia, but no hydronitric acid. The work of Benrath and Ruland[24] upon ceric ion, and that of Bray and Cuy[23] upon manganic and ferric ions show that these oxidants behave in an entirely similar fashion. Manganic ion was found under certain conditions to oxidize hydrazine quantitatively to water, nitrogen and ammonia in conformity with the typical reaction of mono-delectronation.

Prom the theory just outlined it is predictable that ceric ion, in common with all other mono-delectronators studied, would yield no hydronitric acid as a product of the oxidation of hydrazine. Repeated experiments conducted in this Laboratory, under conditions most favorable for the formation and isolation of the acid, yielded no trace of hydronitric acid, thus confirming the work of Benrath and Ruland. Since Sommer and Pincas[25] and Martin[26] have employed ceric ion for the quantitative oxidation of hydronitric acid, however, it might be urged that this action would account for the non-appearance of the acid as a product of the oxidation of hydrazine. Thiele[27] ascribed the relatively low yields of hydronitric

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[22] Minunni, *Gazz. chim. ital.*, [2] 22, 217 (1892); [1] 26,441 (1896); v. Pechmann, *Ber.*, *26*, 1045 (1893); 27,2920 (1894).

[23] Bray and Cuy, THIS JOURNAL, 46,1810 (1924).

[24] Benrath and Ruland, Z. *anorg. Chem.*, 114,267 (1920).

[25] Sommer and Pincas, *Ber.*, 48, 1963 (1915).

[26] Martin, THIS JOURNAL, 49,2133 (1927).

[27] Thiele, *Ber.*, 41,2681,2806 (1908).

acid obtained in various reactions to the "easy oxidizability (leichten Oxydierbarkeit)" of the acid. This suggestion was effectually nullified by the work of Riegger.[28] Nevertheless, it has seemed desirable to obtain direct evidence for the case of the interaction of ceric and hydrazine ions, as to whether putative traces of hydronitric acid would escape oxidation by the ceric ion under the prevailing conditions.

Known amounts of hydronitric acid were introduced beneath the surface of a boiling mixture of ceric sulfate and sulfuric acid in various concentrations. Amounts as small as 0.0001 g. were found to pass through the solution without appreciable loss. This justifies the conclusion that the non-appearance of the acid must be attributed to the inherent character of the reaction, which is clearly one of mono-delectronation.

Oxidation of **Hydrazine** by **Di-delectronators.**—Hydrazine may be completely oxidized, under suitable conditions, by certain di-delectronators, at least, to nitrogen and water. In case the oxidation by di-delectronators is incomplete, hydronitric acid is also formed, under favorable conditions, and is invariably accompanied by ammonia. It is probable that bivalent N_2H_2 residues, which may be regarded as free radicals containing either two atoms of bivalent nitrogen or one atom of univalent nitrogen, are first formed in accordance with the equation

$$N_2H_5^+ - 2\ominus = N_2H_2 + 3H^+ \tag{3}$$

If this process involves the removal of one electron from each of the nitrogen atoms, the NH.NH radical would be formed; the removal of two electrons from one nitrogen, on the other hand, would yield the $N.NH_2$ radical.[29]

Various types of condensation, involving (a) two of these radicals of the same kind, (b) two of different kinds or (c) one of either kind with a molecule of hydrazine, may be considered to occur. Of the five possible bimolecular types only those will be discussed, however, that would yield compounds of which organic derivatives have been prepared.

Condensation of two $N.NH_2$ radicals would yield symmetrical tetrazene, $NH_2.N{:}N.NH_2$, of which numerous organic derivatives, formerly termed tetrazones, have been described.[30] This intermediate product would readily decompose, yielding molecular nitrogen and hydrazine, as follows

$$N_4H_4 = N_2 + N_2H_4 \tag{4}$$

The formation of nitrogen, primary and secondary amines and aldehydes as decomposition products of the tetra-alkyl tetrazenes, noted by Fischer[31]

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[28] Riegger, This Journal, 33, 1569 (1911).

[29] It is possible that these initial products, instead of being free radicals, as here suggested, may be the much-sought di-imide, NH:NH, and its unsymmetrical isomer, $N{:}NH_2$, of which the azo compounds and the diazonium compounds are derivatives.

[30] For a comprehensive summary of these compounds see Wieland, "Die Hydrazine," Ferd. Enke, Stuttgart, **1913**, p. 38.

[31] Fischer, Ann., **199**, 324 (1879).

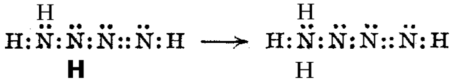
and by **Renouf**,[32] is explained by **Wieland**[33] as a result of the formation and subsequent decomposition of the tetra-alkyl hydrazines.

It is probable that all hydrazine molecules that undergo complete oxidation in acid solution to nitrogen and water pass through the stage represented by Equation 4. The relatively large amounts of nitrogen formed in many of the oxidation reactions studied indicate a preferential oxidation of the $N_2H_5^+$ ion to the unsymmetrical residue, $N.NH_2$, rather than to the symmetrical residue, NH.NH. In the case of mono-delectronators, the tetrazane first formed might yield symmetrical tetrazene on further **oxidation**.[34]

Condensation of two HN.NH radicals might conceivably yield **tetrimide**, $(NH)_4$, as an intermediate product. This seems unlikely, however, in view of the circumstance that no derivatives of this possible compound have yet been described. Condensation with subsequent rearrangement, possibly by way of **aminotri-imide**, as suggested by the work of Wohl and **Schiff**,[35] would result in the formation of unsymmetrical tetrazene, $HN{:}N.NH.NH_2$, of which numerous derivatives, formerly termed **buzylenes**[36] or **diazohydrazines**[35] have been prepared. These substances have long been known to yield derivatives of hydronitric acid and ammonia, and it seems inevitable that unsymmetrical tetrazene itself should decompose in corresponding fashion, in the sense of the equation

$$N_4H_4 = HN_3 + NH_3 \tag{5}$$

This decomposition may result from the migration of one hydrogen nucleus from a central to an external nitrogen atom, as indicated in the diagram[37]



$$H{:}\overset{H}{\ddot{N}}{:}\underset{H}{\ddot{N}}{:}\ddot{N}{::}\ddot{N}{:}H \longrightarrow H{:}\underset{H}{\overset{H}{\ddot{N}}}{:}\ddot{N}{:}\ddot{N}{::}\ddot{N}{:}H$$

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[32] Renouf, Ber., 13, **2169** (1880).

[33] Wieland, Ann., 392, **127 (1912).**

[34] Minunni (ref. **22)** obtained evidence of the existence of a tetrazane of the type RR'N.NH.NH.NRR', which on oxidation yielded the symmetrical tetrazene, **RR'N.N:-N.NRR'.**

[35] Wohl and Schiff, Ber., **33,2741 (1900).**

[36] **Curtius,** Ber., 29,759 (1896).

[37] The use of the conventional electronic diagrams as a convenient device for picturing such molecular rearrangements is not to be construed as an acceptance by the authors of the possible implication that hydronitric acid is a non-polar compound, or that the valence of nitrogen, in any ordinary sense of the term, may be two and four in this compound [**Langmuir, THIS JOURNAL,** 41, **1543 (1919)].** On the basis of both experimental and theoretical considerations the acid may better be regarded as a polar compound, in which the central nitrogen atom tends to relinquish its five valence electrons, yielding three to the external nitrogen atom and two to the **imino** group. This finds expression in the formula $H\rightarrow N\leftleftarrows N\Rrightarrow N$. The N_3^- ion, either in solution or in the crystal lattice of the metallic **trinitrides,** should possess a symmetrical structure, and the nucleus of the central atom should be equidistant from the nuclei of the outer atoms, each

This would be tantamount to the formation of a labile molecular compound of ammonia and hydronitric acid, $HN_3.NH_3$, isomeric with ammonium trinitride.[38]

Condensation of one $N.NH_2$ with one HN.NH radical and subsequent rearrangement would again result in the formation of unsymmetrical tetrazene, which decomposes in the manner expressed by Equation 5.

Condensation of one $N.NH_2$ or of one HN.NH radical with a molecule of hydrazine should yield, after simple rearrangement, a molecule of tetrazane, which would decompose with formation of nitrogen and ammonia in accordance with Equation 2. This affords a satisfactory explanation of the fact that larger yields of ammonia than of hydronitric acid have been invariably obtained in the oxidation of hydrazine.

Among the di-delectronators previously studied in this Laboratory[1] are peroxide, persulfate, chlorate, bromate, iodate, arsenate, antimonate, selenate, tellurate and molybdate ions. Each of these has been found to oxidize hydrazine under suitable conditions[39] with formation of water, nitrogen, hydronitric acid and ammonia. The reaction of hydrogen peroxide upon hydrazine sulfate has been employed by Browne and Lundell[40] in this Laboratory, and by Martin[26] in the preparation of very pure hydronitric acid.

These experiments attest the validity of the classification, here proposed, for oxidizing agents that have already been investigated. The question now arises as to whether the theory will be of use as a means of predicting the behavior of hitherto unstudied di-delectronators.

Oxidation of Hydrazine by the Di-delectronator, Chlorauric Acid.—It was shown by Lenher[41] that chlorauric acid is reduced by hydrazine, with formation of metallic gold. Gutbier[42] employed hydrazine, and Gutbier and Resenscheck[43] phenylhydrazine in the preparation of gold hydrosols of different colors. No attempt seems to have been made by these investigators to ascertain whether or not hydronitric acid (or phenyl azide) was formed as a product of the reaction.

A solution of chlorauric acid was prepared by dissolving 0.8 g. of gold in aqua regia. Since the presence of oxides, oxy-acids, or oxychlorides

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of which is furnished with eight electrons. This is in conformity with the recent work of Hendricks and Pauling [This Journal, 47, 2904 (1925)] upon the crystal structure of potassium and sodium trinitrides, but contradicts the statement of Carothers [This Journal, 45, 1734 (1923)] that "the structure $R-N=N\equiv N$ is, of course, impossible from the point of view of the octet theory."

[38] Ref. 1 h, p. 288, footnote 1.

[39] In the case of iodate ion no hydronitric acid is formed unless silver sulfate, which serves to prevent the liberation of iodine, is present.

[40] Browne and Lundell, This Journal, 31, 435 (1909).

[41] Lenher, *ibid.*, 35, 546 (1.913).

[42] Gutbier, *Z. anorg. Chem.*, 31, 448 (1902).

[43] Gutbier and Resenscheck, *ibid.*, 39, 112 (1904).

of nitrogen might result in the formation of hydronitric acid from hydrazine, thus masking the possible effect of the reagent, scrupulous care was taken to eliminate the last traces of these substances. The purified solution, diluted to 100 cc., was slowly introduced beneath the surface of a 200cc. portion of a boiling, 0.5% solution of hydrazine sulfate. In two experiments, in which a considerable excess of unoxidized hydrazine remained in the distilling flask, yields of 0.006 and 0.004 g. of hydronitric acid were obtained. The chlorauric acid was quantitatively reduced to metallic gold. The presence of ammonia in the residual solutions was established by qualitative tests.

The formation of hydronitric acid under the conditions just described, which were by no means the most favorable for its production, unequivocally fulfils the prediction concerning the behavior of chlorauric acid. The smallness of the yields is attributable to various factors, including (1) the relatively low concentration of sulfuric acid, (2) the momentary liberation of chlorine during the reaction and (3) the action of aurous ion as *a* mono-delectronator.

Complex Delectronators.—Oxidizing agents that undergo reduction in two or more stages may in certain cases manifest the characteristics of a mixture of mono- and di-delectronators. The course of the reduction would then be a resultant of the reactions of both types. In such cases it should theoretically be possible, by the use of suitable addition agents, wholly or in part to eliminate one type of reaction, or the other, thus rectifying the complex delectronator, by virtually converting it into a simple mono- or di-delectronator.

An indubitable instance of such rectification is afforded by the work done in this Laboratory[1"] upon the reaction between iodate ion and hydrazine ion in acid solution. This reaction yields iodide ion, readily oxidizable by iodate with liberation of iodine, which in monatomic form is a mono-delectronator. The reaction between iodine and hydrazine evidently takes precedence over that between iodate and hydrazine, with the result that no hydronitric acid is formed. The addition agent, silver sulfate, however, effects removal of the iodide, leaving the iodate ion free to act upon the hydrazine with formation of both hydronitric acid and ammonia.

In case each of the possible stages of a reaction involves simply an accession to the oxidant of the two electrons, the reaction would clearly be one of simple di-delectronation. If, on the other hand, any one of the stages consists in the transfer of a single electron, the reaction is one of complex delectronation.

Potassium permanganate, in its behavior toward hydrazine, affords another instance of complex delectronation. Browne and Shetterly[1d] found that small amounts of hydronitric acid and large amounts of ammonia were formed by the interaction of permanganate and hydrazine ions in acid solution. Since the yields of ammonia were considerably in excess of the values required by Equation 5, the conclusion may be drawn that the principal reaction, aside from that expressed in Equation 4, is one of mono-delectronation, as represented by Equations 1 and 2. This points toward manganic ion, readily formed by interaction of manganous and permanganate ions, as the principal agent. This conclusion is strongly confirmed by the work of Bray and Cuy.[3,23] Any addition agent that would reduce the concentration of manganic ion should increase the yield of hydronitric acid by rectifying the complex reaction to one of simple di-delectronation.[44]

Oxidation of Hydrazine by the Complex Delectronator, Ammonium Metavanadate.—From the work already done in this Laboratory[1b] upon the action of ammonium metavanadate in acid solution upon hydrazine, it is apparent that this reaction is not one of simple di-delectronation. Indeed, at first glance, it would appear, apart from the evidence of the formation of hydronitric acid, to be one of simple mono-delectronation involving reduction of trivalent vanadyl ion (quinquivalent vanadium) to bivalent vanadyl ion (quadrivalent vanadium), as follows

$$VO^{+++} + \ominus = VO^{++} \qquad (6)$$

It is probable, however, as suggested by Ditz and Bardach[45] for the reaction between vanadates and hydriodic acid, that a part of the quinquivalent vanadium is directly reduced to trivalent vanadium (univalent vanadyl ion), as follows

$$VO^{+++} + 2\ominus = VO^{+} \qquad (7)$$

In this reaction the trivalent vanadyl ion acts as a di-delectronator and is responsible for the formation of hydronitric acid.

It has been shown by the work of Gooch and Gilbert[46] that silver sulfate is reduced by vanadium with a valence of one, two or three, but is not reduced by vanadium with a valence higher than three. The presence of silver sulfate in a reacting mixture of hydrazine and ammonium metavanadate therefore serves to indicate whether or not the vanadium has been reduced below the quadrivalent stage. Metallic silver appears as a product of the reaction in every case where hydronitric acid is formed, and in no case where the acid is not formed. Unless the reduction proceeds beyond the stage represented by Equation 6, therefore, no hydronitric acid is obtained. In a second series of experiments it was found that diminution in the acidity of the solution favors mono-delectronation (Equation 6) and retards di-delectronation (Equation 7), until in a barely acid solution no hydronitric acid whatever is obtained.

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[44] It is possible that addition of soluble sulfates or fluorides for example would produce this result.

[45] Ditz and Bardach, Z. *anorg. Chem.*, **93**, 97 (1915).

[46] Gooch and Gilbert, Am. J. *Sci.*, [4] 15,389 (1903).

Oxidation of Hydrazine by Chlorine, Bromine and Iodine.—In the nascent or monatomic condition the halogens are without doubt to be classified as mono-delectronators. Under such conditions that the diatomic molecules, the positive ions (Cl^+, Br^+, I^+), or the ions of the hypo-acids (OCl^-, OBr^-, OI^-) constitute the active units, however, the halogens should be capable of functioning as di-delectronators. Earlier observations" of the formation of small amounts of hydronitric acid from hydrazine by the action of chlorine and bromine confirm this supposition. The issue is complicated, however, by the possibility that halogenation may occur, with formation of halogenated residues as intermediate products, which may behave very differently from the radicals liberated by other oxidizing agents.

Chattaway[47] has investigated the action of chlorine and of bromine upon certain primary aromatic hydrazines, and has obtained various halogen substitution products of these substances. In so far as the decomposition of these compounds has been studied it would appear strictly analogous to the decomposition of the corresponding derivatives of free hydrazine to form nitrogen gas and hydrogen chloride.

Despite the probable predominance of halogenation in the oxidation of hydrazine by the free halogens, small amounts of hydronitric acid and ammonia may nevertheless be obtained under suitable conditions, indicating that di-delectronation must occur to some extent during the process.

Experiments in which freshly prepared chlorine water was introduced beneath the surface of a boiling 1% solution of hydrazine sulfate containing one-half of its volume of concentrated sulfuric acid, yielded appreciable amounts of hydronitric acid and ammonia, both in the absence and in the presence of silver sulfate. With bromine smaller yields, found to vary directly with the concentration of the sulfuric acid and to increase in the presence of silver sulfate, were obtained.

With iodine detectable amounts of hydronitric acid were formed only in the presence of silver sulfate. The probable effect of the addition of silver sulfate is to reduce the concentration of iodide ion and thus to favor the formation of iodous ions (I^+). Increase in the acidity of the solution would undoubtedly produce the same effect. The iodous ion, obviously a di-delectronator, is capable of yielding hydronitric acid under favorable conditions, but the necessarily low concentration of the ion precludes the formation of more than small amounts of this product.

Summary

A classification of oxidizing agents (and reducing agents) has been suggested on the basis of the number of electrons transferred per active unit.

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[47] Chattaway, *J. Chem. Soc.*, 93, 852 (1908); 95, 1065 (1909).

The hitherto unaccountable similarity in the behavior of various oxidants of widely divergent potentials toward hydrazine is now explained on the ground that they are either *mono-delectronators,* yielding ammonia as the only by-product of the reaction, or *di-delectronators,* yielding both ammonia and hydronitric acid.

Further applications of this idea are projected, particularly for the case of other oxidation-reduction reactions in the fields of inorganic and organic chemistry in which intermediate products are formed.

ITHACA, NEW YORK

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

MICELLES AND THE ACTIVITY COEFFICIENT IN ALKALI SILICATE SOLUTIONS

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The theory of colloidal electrolytes as used by McBain[1] postulates the replacement of a simple ion formed by the dissociation of an electrolyte, by a heavily hydrated polyvalent micelle or ion "which carries the equivalent sum-total of electrical charges" of the ions which it replaces. This theory was carefully considered by McBain and Salmon,[2] and by McBain, Laing and Titley,[3] who determined the dew point lowering and freezing point lowering of soap solutions. And from their data, Randall, McBain and White[4] calculated the activity coefficients.

McBain and Salmon[2] predicted that solutions of sodium silicate and certain other salts of the heavy metals, as well as the soaps, would be found to contain varying quantities of micelles. Recently, Harman[5] has postulated on the basis of his freezing point measurements, the existence of micelles in concentrated sodium silicate solutions containing a large excess of silica.

Before considering the constitution of the alkali silicate solutions as determined by their colligative properties, we will examine the significance of the activity coefficient of a solution in which micelles may be formed.

The Activity Coefficient in Solutions Containing Micelles

The activity of a solute is the ratio of the escaping tendency, or fugacity, of that constituent of a solution divided by the escaping tendency of the constituent in some standard state which is arbitrarily chosen.[6] The escaping tendency is, of course, independent of any assumed constitution

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[1] (a) McBain, *Trans. Faraday Soc.*, 9, 99 (1913); (b) *Kolloid Z.*, 12,256 (1913).

[2] McBain and Salmon, THIS JOURNAL, 42,426 (1920).

[3] McBain, Laing and Titley, *J. Chem. Soc.*, 115,1289 (1919).

[4] Randall, McBain and White, THIS JOURNAL, 48,2517 (1926).

[5] Harman, *J. Phys. Chem.*, 31,355 (1927).

[6] See Randall, *Trans. Faraday Soc.*, 23,498 (1927).

of the solute. For convenience, when dealing with electrolytes, the chosen standard state is defined with reference to the infinitely dilute solution, and the activity is taken equal to the product of the activities of the ions into which the electrolyte is assumed to dissociate.[7] The activity coefficient of an ion is the number by which the stoichiometrical molality of the ion is multiplied to obtain the activity, and the activity coefficient of the solute is the geometrical mean of the activity coefficients of the ions.

We shall consider a solute in which the negative ions of a uni-univalent strong electrolyte are replaced by ionic micelles. Let us call m the molality of the solute AB, and n the number of univalent negative ions which unite to form an ionic micelle. The molality of the positive ion constituent is also m. If the negative ion constituent is present only in the form $(B_n)^{n-}$, then the molality of the solute and also the molality of the micelle ion is $m' = m/n$. Neglecting the hydration,[6] we may write

$$A_nB_n = nA^+ + (B_n)^{n-};\ a_2 = a_+{}^n a_- \qquad (1)$$

where a_2 is the activity of the solute, and a_+ and a_- are the activities of the positive ion and negative micelle, respectively. For the mean molality, we find

$$m_\pm = (m_\pm{}^n m')^{1/(n+1)} = m_+/n^{1/(n+1)} \qquad (2)$$

From Equation 2, we see that as n becomes a very large number, the mean molality of the ions becomes nearly equal to the molality of the positive ion constituent. Or, if n is infinite, we should say that the whole of the solute was a single particle, possessing the entire negative charge of the solution, surrounded by the univalent positive ions. If all the ions obeyed the law of the perfect solution, then the freezing point lowering of such a solute would be the same as that of a non-electrolyte having the same molality as that of the positive ion constituent. Consequently, in the limit, when n becomes very large, ν, the number of ions produced by the dissociation of each molecule of AB, approaches unity. Following the treatment by Bjerrum,[8] we should expect a micelle as formulated in Equation 1 to be a progressively weaker electrolyte as the value of n is increased. In the limit, when n becomes very large, perhaps the micelle would no longer behave as an electrolyte. We shall show in a later section that the micelles of sodium acid silicate behave as slightly weak electrolytes. The un-ionized micelles postulated by McBain and Salmon[2] can possibly be explained in this way.

In the ordinary manner, we have the ionic strength of the solution

$$\mu = (m_+ + m'n^2)/2 = m_+(n + 1)/2 \qquad (3)$$

As n increases, the ionic strength rapidly increases and becomes infinity in the limit when n becomes infinite.

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[7] See Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chap. XXVI.

[8] Bjerrum, *Kgl. Danske Videnskab. Selskab Math.-fys. Medd.*, 7, No. 9 (1926).

The activity coefficient of a solute is proportional to the square root of the ionic strength. If the solution is completely dissociated, the activity coefficient for a given ionic strength will be less, the greater[9] the value of n. The "association" in the Bjerrum[8] sense would still further reduce the expected activity coefficient of the micelles.

In the discussion of the activity coefficient of soaps by Randall, McBain and White,[4] the activity of the solute was set equal to the square of the product of the stoichiometrical molality and the activity coefficient, and we shall adopt the same convention in discussing the sodium acid silicates. Although, if for purposes of formulating a mechanism which will explain the divergence of the activity coefficients of these substances from those of typical uni-univalent electrolytes, we assume the existence of micelles, this device is in no way essential to the thermodynamic treatment. We selected as the solutes[6] the sodium ion and hydrosilicate ion, or sodium ion and univalent soap ion, because they were simple, and because in the dilute solution the behavior of the electrolytes was the same as that of typical electrolytes. The actual molality of the various ionic micelles, or of the various hydrates, or of the neutral micelles, or of undissociated substances is unknown; but their fugacity is the same as that of the solutes arbitrarily chosen, for they are in equilibrium with these substances. As long as no solute molecule is present whose composition cannot be expressed in terms of the ions chosen as solutes, and as long as these substances are in equilibrium, it is immaterial which of the species is chosen as the solute. Accordingly, the species with the simplest formula is used.

In the case of the hydrolysis of one of the ions, as that of SiO_3^{--}, the case is different, for the composition of the products of hydrolysis cannot be expressed in terms of the ions formed from the chosen solute. But, by drawing the curve as we shall do in Fig. 1, we assume that the curve as drawn is the curve which would be given by a substance of this nature if no hydrolysis occurred. Therefore, in taking the area under the curve, we obtain, with no great error, the activity coefficient of the normal silicate, without hydrolysis.

We shall now consider the various experimental determinations of the freezing point lowering,[10] vapor pressure lowering,[10a] dew point lowering[11] and boiling point raising[12] of the various sodium silicate solutions.

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[9] See Bronsted, *Trans. Faraday Soc.*, 23, 416 (1927), who reviews the earlier literature.

[10] (a) Harman, J. *Phys. Chem.*, 31, 355 (1927); (b) Kahlenberg and Lincoln, *ibid.*, 2, 77 (1898), also Li, K, Rb and Cs silicates; (c) Loomis, *Phys. Rev.*, [1] *4*, 273 (1897); *Ann. Physik. Chem.*, [3] *60*, 523 (1897); (d) Thompson, Manuscript Thesis, Worcester Polytechnic Institute, Worcester, Mass., 1923.

[11] Bennett, J. *Phys. Chem.*, 31, 890 (1927).

[12] (a) Cann and Cheek, *Ind. Eng. Chem.*, 17, 612 (1926); (b) Cann and Gilmore, *J. Phys. Chem.*, 32, *No.* 1 (1928).

Activity Coefficient of Sodium Silicate Solutions

Harman,[10a] Bennett[11] and Cann and Gilmore,[12b] took the molality of their silicate solutions equal to twice the molality of the sodium ion constituent. Numerous investigators[13] have shown that hydrolysis of the solutions is increased with dilution and with increase of temperature. For this reason, Harman,[10a] Bennett[11] and Cann and Gilmore,[12b] took the value of ν in the freezing point equation of Lewis and Randall[7] equal to 4, for solutions of all ratios of Na_2O to SiO_2. They then calculated the activity coefficients of the various solutions by the methods of Lewis and Randall.? Their calculations tacitly assume for the reaction

$$Na_2SiO_3\,(aq) + H_2O\,(l) = 2Na^+ + OH^- + HSiO_3^- \qquad (4)$$

$K = 1$, in accordance with the conventions adopted by Lewis and Randall in developing the basic equations used. In other words the activity of the sodium silicate is made equal to the geometric product of the activities of the ions on the right of Equation 4.

In a later paper, Harman[14] calculated the two dissociation constants of metasilicic acid from electrometric titration curves. His curves show definitely two "breaks" such as are found when sodium carbonate is titrated with hydrochloric acid.

We have recalculated the values of the activity functions[15] $h/m^{1/2}$ and $j/m^{1/2}$ for all the above measurements. We have used $\nu = 3$ for ratios of 1:1 of Na_2O to SiO_2 and $\nu = 2$ for ratios of 1:2 to 1:5. In the latter case, the molality was taken equal to the number of gram atoms of sodium ion constituent. These assumptions correspond to $K = 1$ for the reactions

$$Na_2SiO_3\,(aq) = 2Na^+ + SiO_3^{--} \qquad (5)$$
$$NaHSiO_3\,(aq) = Na^+ + HSiO_3^- \qquad (6)$$

It has been impossible to eliminate the effect of hydrolysis, but in the concentrated solutions this effect cannot be large,[13] and the method of extrapolation here used eliminates to a great extent the effect in the more dilute solutions.

Sodium Metasilicate.—The values of $j/m^{1/2}$ and $h/m^{1/2}$ for the various silicates containing $1Na_2O{:}1SiO_2$ are shown plotted against the square root of the molality in Fig. 1. The average values of $j/m^{1/2}$ for barium

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[13] (a) Kohlrausch, *Z. physik. Chem.*, 12, 773 (1893); see also (b) Bogue, THIS JOURNAL, 42, 2575 (1920); (c) Cann and Cheek, ref. 12a; (d) Harman, *J. Phys. Chem.*, 29, 1155 (1925); (e) *ibid.*, 30, 359 (1926); (f) *ibid.*, 30, 917 (1926); (g) *ibid.*, 30, 1100 (1926); (h) *ibid.*, 31, 355 (1927); (i) Kahlenberg and Lincoln, ref. 10b; (j) Loomis, ref. 10c; (k) Thompson, ref. 10d.

[14] Harman, *J. Phys. Chem.*, 31,616 (1927).

[15] (a) Randall, THIS JOURNAL, 48, 2512 (1926); (b) Randall and White, *ibid.*, 48, 2514 (1926); (c) Randall, *Trans. Faraday Soc.*, 23, 502 (1927); $j = 1 - (\theta/\nu\lambda m)$, where θ is the freezing-point lowering, ν the number of ions formed from one molecule, $\lambda = 1.858$, the freezing-point constant and m the molality; $h = 1 + (55.51 \ln a_1)/\nu m$, where a_1 is the activity of the solvent.

nitrate[16] are shown as the dotted curve. Fig. 1 also shows for comparison the values of $j/m^{1/2}$ for the ratio Na_2O:1.4SiO_2, if we assume the molality equal to the moles of Na_2O and $v = 3$.

The effect of hydrolysis is seen in the negative values of $j/m^{1/2}$ and $h/m^{1/2}$ which, for a hydrolyzed substance will approach $-\infty$ at infinite dilution. In molal solution the hydrolysis is not large and we gain an idea of the activity coefficient of sodium silicate, when defined in accordance with Equation 5, by drawing the solid curve, to follow the general direction of the curve for barium nitrate. The activity coefficient of the normal sodium silicate as calculated by the equation

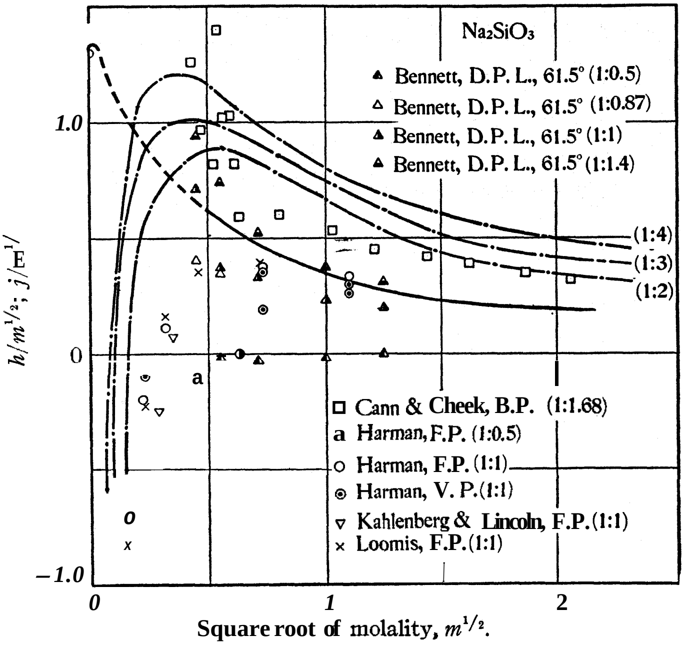

Fig. 1.—Activity function of sodium metasilicate.

$$\log \gamma = -j/2.303 - (2/2.303) \int_0^m (j/m^{1/2}) dm^{1/2} \qquad (7)$$

for round molalities is shown in the second row of Table I. The temperature coefficient of the activity coefficient has been neglected and the values are approximate for any temperature between 0 and 100".

TABLE I

ACTIVITY COEFFICIENTS OF SODIUM METASILICATE SOLUTIONS, Na_2SiO_3

m	0.05	0.10	020	050	1.00	200
γ	.501	.408	.318	.232	.182	.141

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[16] Randall and Scott, THIS JOURNAL, 49, 647 (1927).

The neutral sodium silicate is about as weak, that is, has the same activity coefficient, as barium nitrate, which was shown by Randall and Scott[16] to be weaker than typical strong electrolytes of the same valence type. We should, therefore, expect a slight "association" in the Bjerrum[8] sense, but such an effect is not apparent in the values of $j/m^{1/2}$, because of the large hydrolysis.

Our activity coefficient represents approximately the mean activity coefficient of the Na^+ and unhydrolyzed SiO_3^{--} ions present in any solution of an ionic strength three times the molality given in Row 1, when we assume the principle of the ionic strength.

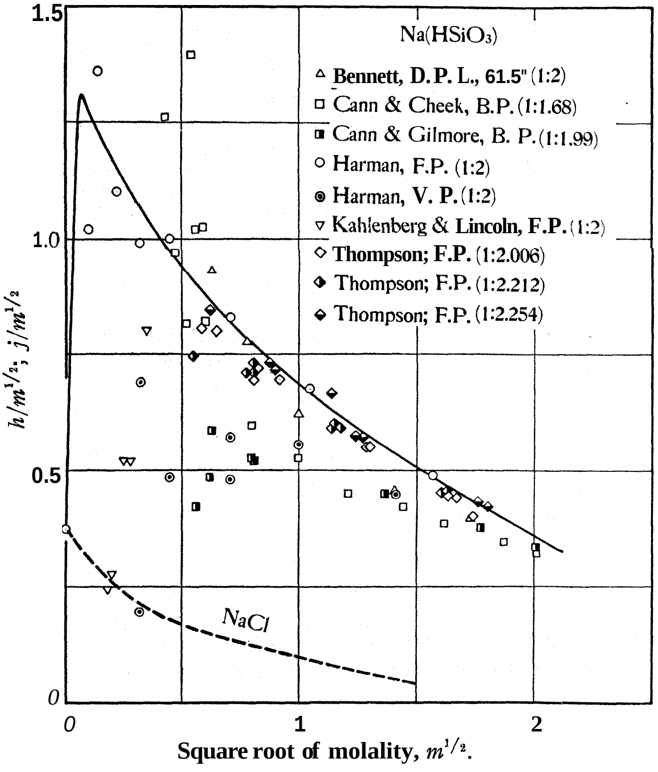

Fig. 2.—Activity function of sodium acid silicate.

Sodium Acid Silicates.—The values of $j/m^{1/2}$ and $h/m^{1/2}$ for the various silicates with ratios $1Na_2O{:}1.68SiO_2$ to $1Na_2O{:}2SiO_2$ are shown in **Fig.** 2; those for ratios $1Na_2O{:}2.55SiO_2$ to $1Na_2O{:}3SiO_2$ are shown in Fig. 3; those for ratios $1Na_2O{:}3.154SiO_2$ to $1Na_2O{:}5SiO_2$ are given in Fig. 4. The molality is that of sodium ion constituent and the acid silicates have been assumed to dissociate in accordance with Equation 6. The silica in excess of 2 moles of SiO_2 per Na_2O has been assumed to be combined in the univalent negative ion. Fig. 2 also shows as a dotted curve the average values of $j/m^{1/2}$ for sodium chloride.

The curves of Figs. 2 to 4 are similar to those obtained for moderately strong acids, such as dichloro-acetic. No typical uni-univalent salts, such as the uni-bivalent cadmium chloride or mercuric chloride, with low activity coefficients, have been noted, although one of us has plotted the values of $j/m^{1/2}$ and $h/m^{1/2}$ for all published measurements.

Randall, McBain and White[4] plotted the values of $j/m^{1/2}$ and $h/m^{1/2}$ for the various sodium and potassium soap solutions. In the dilute solutions the values appear to be about the same as those for potassium chloride. At a concentration of about 0.05 M for a soap with a large number of carbon atoms to about 0.3 M for a soap with a small number, the values of $j/m^{1/2}$ begin to increase (log γ to decrease), the increase becoming larger, the greater the molecular weight of the soap. This rise is at the concentration in which micelles were assumed to begin to form as determined by conductance, viscosity and other data. The curves of Figs. 2 to 4 resemble the portions of the plots[4] of the data for the soaps in the higher concentrations. If the data are to be considered reliable, there is no evidence of behavior like that of sodium chloride in dilute solutions, and if the silicates give a rapid rise in the $j/m^{1/2}$ curve, as in the soap solutions, then this rise occurs in much more dilute solutions.

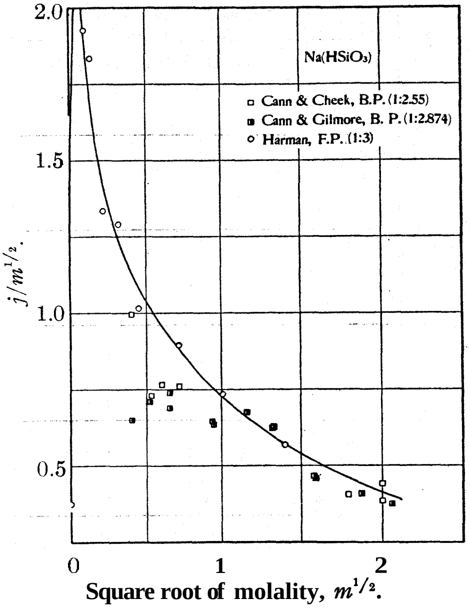

Fig. 3.—Activity function of sodium acid silicate.

Micelles can be assumed to form according to the equation

$$n(\mathrm{HSiO_3}\cdot y\mathrm{SiO_2}\cdot z\mathrm{H_2O^-}) = [r\mathrm{HSiO_3}\cdot s\mathrm{SiO_2}\cdot w\mathrm{H_2O}]^{n-} + x\mathrm{H_2O} \quad (8)$$

in which molecules of monovalent hydrosilicate ion with an indefinite amount of added water and silica unite to form the micelle with n negative charges and a new indefinite amount of water and silica of solvation. All of the silica will presumably remain in the micelle. The value of n may be a fairly large constant number, or it may vary with the concentration. We can confidently expect that in the infinitely dilute solution, the micelles will be completely dissociated or hydrolyzed, in which case $j/m^{1/2}$ will approach the same limit as typical uni-univalent electrolytes, just as

Bjerrum[8] has assumed for the behavior of partly associated substances. If the micelles persist to a sufficiently low concentration, then there will appear no such minimum in the $j/m^{1/2}$ curves as was found in the case of the soaps, and we may draw our average curve, somewhat as shown in Figs. 2 to 4. The approximate activity coefficients as calculated from these curves for the various ratios are shown in Table II.

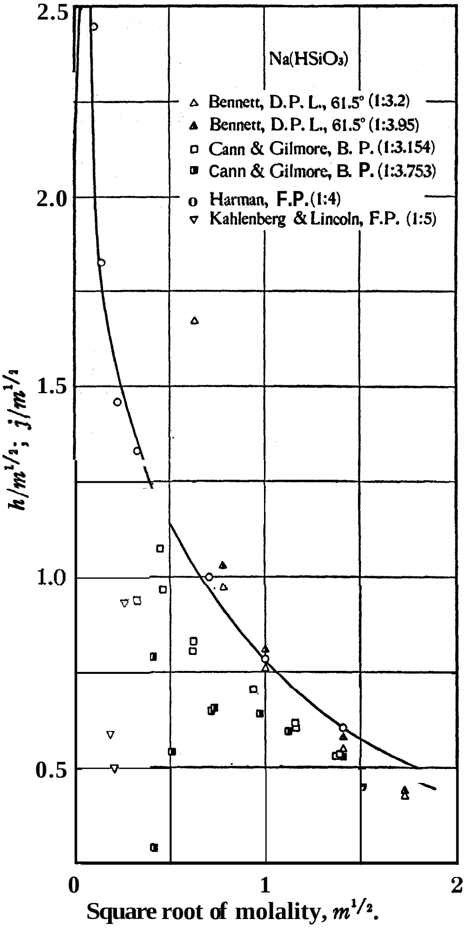

Fig. 4.—Activity function of sodium acid silicate.

The existence[17] of crystalline salts of the type $Na_2Si_2O_5$ is cited as an argument for the existence of $Si_2O_5^{--}$ in solution. The acid salt, $KHSi_2O_5$,[17b] has been prepared. However, the existence or non-existence of a crystalline salt does not necessarily indicate the presence of a considerable amount of the corresponding ions in solution, for they may react with the water, or may be in rapid equilibrium with an ion such as $HSiO_3^-$. Silicate solutions are known to change their thermodynamic properties with time, and some of these reactions may be slow. In the case of the measurements used in Figs. 1 to 4, a sufficient time to reach a stable state elapsed.

The broken curves of Fig. 1 show the average curves which correspond to the final mean curves taken from Figs. 2 to 4, when the molality of the acid silicates is taken as equal to one-half that of the sodium ion constituent and the divalent hydrated $Si_2O_5^{--}$ is assumed to be the principal negative constituent of the solutions. The excess silica is assumed to be combined in this negative ion in a way similar to that used in the former consideration of univalent $HSiO_3^-$. The values of $j/m^{1/2}$ for the acid sili-

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[17] (a) Niggli, THIS JOURNAL, 35, 1693 (1913); (b) Morey, *ibid.*, 36, 215 (1914); (c) Morey and Bowen, *J. Phys. Chem.*, 28, 1169 (1924); (d) Thompson, ref. 10 d; (e) Harman, *J. Phys. Chem.*, 31, 511 (1927); see also (f) Jordis, *Z. anorg. Chem.*, 56, 305 (1907); (g) Westerberg, *Z. anorg. Chem.*, 88, 341 (1915).

TABLE II

ACTIVITY COEFFICIENTS OF SODIUM ACID SILICATE SOLUTIONS, $Na(HSiO_3)$

m	(1:2)	(1:3)	(1:4)
0.05	0.464	0.341	0.268
.10	.347	.247	.187
.20	.246	.169	.121
.50	.131	.088	.060
1.00	.076	.049	.033
2.00	.043	.027	.017
4.00	.027	.015	.008

cates, calculated on the basis of $\nu = 3$, ($Na_2Si_2O_5$), show a larger number of negative values in the dilute solutions than those calculated on the basis of $v = 2$, and this may be taken as an argument for the use of our convention.

Since the curves of Figs. 2 to 4 can be explained by assuming the existence of micelles, we will study the solutions of the highest silica-sodium oxide ratios on the basis of the limiting case, that the number of charges upon the micelles is very large. But before proceeding, we will digress to consider the freezing point function in a mixture of electrolytes.

The Freezing Point Function in Mixtures

If, for any particular type of electrolyte, the values of $j/m^{1/2}$, or $h/m^{1/2}$, are divided by the value of the limit[15a] (at the temperature considered) at zero molality ($j^{\circ}/m^{\circ 1/2}$), and these numbers are plotted against the square root of the molality, as in Fig. 5, the curves for all strong electrolytes of the various valence types will coincide if the effect of the size of the ions, hydration, etc., is the same.[18]

The function j is a property of the solvent. We may imagine the lowering of the freezing point to be the sum of the partial lowerings caused by each of the several constituents of a mixed electrolyte, such that $j = j_2 + j_3 + \ldots$. The value of $j_2/m_2^{1/2}$ or of $j_3/m_3^{1/2}$ will approach the same limit at infinite dilution as that approached by $j/m^{1/2}$ for a pure substance of the same valence type, but will depend upon the value of the ionic strength of the solution, rather than upon the molality of the particular constituent. If there is a common ion we must consider the function $j_2/m_{2\pm}^{1/2}$; but it is obvious from the definition[15] of j that if $m_{\pm}$ is substituted for m, then the sum of the various partial values of j will be greater than the total j. If the principle of the ionic strength is obeyed, then we should expect the curve of $(j_2/m_{2\pm}^{1/2})/(j_2^{\circ}/m_{2\pm}^{\circ 1/2})$ to be identical with the curve of Fig. 5.

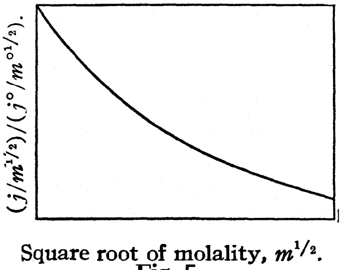

Fig. 5.

The assumptions of the previous paragraph do not enable us to determine

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[18] Unpublished summary of colligative properties.

the activity coefficient of the several constituents of a mixture, nor the individual activity coefficients of the ions, for the division of the effect of the ions can only be made if we know the individual activities of the solutes. The idea, however, with the assumption of the principle of the ionic strength, enables us to examine qualitatively such curves as those of Fig. 6.

Micelles and Activity Coefficient of Sodium Ion

If a considerable portion of the hydrosilicate is in the form of large micelles, then in fact only one ion is formed per molecule of $NaHSiO_3$ dissociated, namely, a sodium ion; and the value of ν in the freezing point equation is one. We show the values of $j/m^{1/2}$ and $h/m^{1/2}$ calculated on this basis in Fig. 6. The limit at zero molality of $j/m^{1/2}$ for the freezing point measurements will be the same as that for uni-univalent substances, namely, 0.375, and if the usual assumptions[7] in estimating an individual ion activity are made, then the values should vary with the square root of the molality in about the same way as those for sodium chloride.

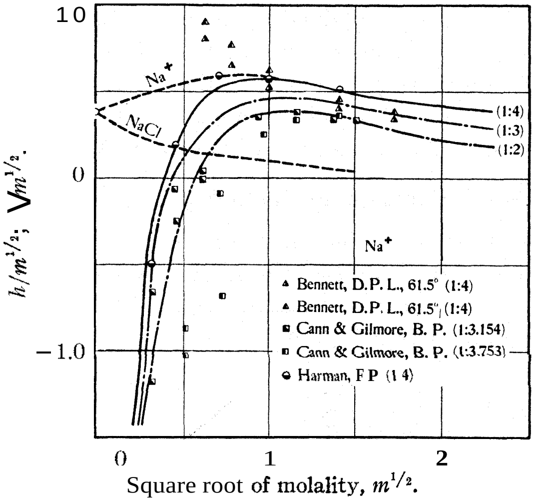

Fig. 6.—Activity function of sodium acid silicate.

Because of the very large charge upon the micelles, and the contribution to the ionic strength of a solution of these large ions, the scale of abscissas should be stretched to the right, and the values of $j_+/m_+^{1/2}$ should appear to decrease much less rapidly than those of sodium chloride. On the other hand, the presence of the large negative ions will cause an association in the Bjerrum[8] sense, because of the much larger distance of minimum approach of the centers of the charges, for complete dissociation, the effect of which would be shown in large values of $j/m^{1/2}$.

Below about 0.3 M the values of $j/m^{1/2}$ on the basis of $\nu = 1$ are in most cases negative, which is to be expected if the micelles dissociate to such an extent that the average number of ions formed per molecule is much greater than one.

We also show in Fig. 6 the values of $j/m^{1/2}$ calculated from the values of the freezing point lowering corresponding to the smoothed curves of Figs. 2 to 4. The values from the curves become negative at higher concentrations, the lower the silica-sodium oxide ratio in the silicates. This may be interpreted as indicating, as is also evident from the curves of Figs. 2 to 4, that the size and number of the micelles is less in the solutions of lower ratios.

The charge of the micelle, if we arc to explain the effects in this way, is greater, the greater the silica content of the negative constituent. The activity coefficient of the sodium ion, basis $v = 1$, is smaller $(j/m^{1/2}$ is larger) in accordance with the idea that the Bjerrum "minimum approach" is larger and "association" therefore greater. Further, we should expect the size of the micelle containing a given number of charges to be greater the greater the relative silica content; therefore the micelle which would have a certain charge density upon its surface (surface/charge) would have a greater number of charges.

In a very real sense the assumption that the ions existing in acid silica solutions are $Si_2O_5^{--}$ or some hydrated multiple thereof may be considered as the first stage in the formation of a micelle, for undoubtedly the negative constituent consists of many different sorts of micelles all in equilibrium (more or less rapid) with each other. But, as we do not have a method of picking out the concentrations of the individual species of micelles, we may as well take $HSiO_3^-$ just as we do in the case of water when we choose H_2O as the species to represent this substance.

Unfortunately, we are unable to fully interpret Harman's[13f] measurements with the sodium amalgam electrode, as the original data are not given and the correction for liquid potential used by him is uncertain. The values in the dilute solutions are the least valuable but the data in concentrated solutions indicate qualitatively that the activity of the sodium ion is smaller, at a given concentration, the higher the silica-sodium oxide ratio. This is in accord with the observations given in a previous paragraph.

All the micelles referred to have been considered to be ionic micelles. McBain and Salmon[2] postulate both ionic and neutral micelles. It is possible that the distinction between the two forms is the same as that between the "associated" (Bjerrum) barium nitrate[16] and the dissociated barium nitrate. There has been no suggestion of the separate existence of neutral (McBain and Salmon) micelles in the silicate solutions.

The results of conductivity measurements and other data do not contradict our explanations.[19]

Summary

1. The theoretical consequences of the choice of the standard state for solutes is considered in relation to the activity coefficient and ionic strength of solutions containing micelles.

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[19] The Editor has kindly called our attention to an article by Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg,* **16,** No. 6 (1926), in which is given a different explanation of the low activity coefficient of such solutions as are here considered.

2. The activity coefficient has been calculated for sodium silicate solutions with various ratios of sodium oxide to silica.

3. Sodium metasilicate solutions behave as typical uni-bivalent electrolytes. The value of ν in the freezing point equation is taken equal to 3 instead of 4 as taken by previous authors. Although sodium metasilicate solutions are largely hydrolyzed, the choice of $\nu = 4$ is not consistent with our conventions regarding the definition of activity coefficients.

4. Sodium acid silicates are not largely hydrolyzed, The formula is taken as $NaHSiO_3$ rather than $Na_2Si_2O_5$, and $\nu = 2$ rather than $\nu = 4$. The acid silicates show extremely low activity coefficients.

5. The low activity coefficients of the acid silicates are explained by the assumption of the existence of ionic micelles which are not entirely dissociated into simple ions except in very dilute solutions.

6. The percentage of substance existing as micelles in the silicates increases with the ratio of silica to sodium oxide.

7. The number of aggregated acid silicate ions forming a micelle increases as the percentage of silica increases.

8. The effect of the ionic micelle upon the individual ion activity of sodium ion is discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

PRIMARY SALT EFFECT IN A ZERO TYPE REACTION

BY MARTIN KILPATRICK, JR.[1]

RECEIVED OCTOBER 27.1927 PUBLISHED FEBRUARY 4, 1928

The present work is a further attempt to distinguish experimentally between the "activity rate theory" and the Brönsted formula for reaction rate in dilute solution.

According to the activity rate theory, the velocity of a reaction between A and B can be expressed by the equation

$$v = ka_Aa_B$$

where a_A and a_B are the activities of A and B, respectively.

Brönsted's[2] general formula may be written

$$v = kc_Ac_B.f_Af_B/f_X$$

where k depends on the temperature and the solvent and f_A, f_B and f_x are the activity coefficients of A, B and the "critical complex," respectively. For a solution so dilute that the activity coefficients of molecules and ions depend only on the charge, the general formula is

$$v = kc_Ac_B.f_{z_A}f_{z_B}/f_{z_A + z_B}$$

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[1] National Research Fellow.

[2] Bronsted, Z. *physik. Chem.*, 102, 169 (1922).

where f_z represents the activity coefficient of an ion of valence z. The effect of salt upon the rate of reaction due to change in the value of the kinetic activity factor, $f_{z_A}f_{z_B}/f_{z_A+z_B}$, is called "primary salt effect." For the case of a reaction between a non-electrolyte and an ion

$$A^0 + B^z \longrightarrow (A,B)^z \longrightarrow \text{products}$$

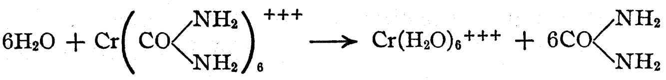
the kinetic activity coefficient becomes f_0f_z/f_z and in dilute solution should have a limiting value of one. The deviation from unity is linear with the concentration and consequently a linear salt effect is expected. According to the activity rate theory an exponential salt effect is predicted, since the rate is considered proportional to the product of the activities of the reactants.

The results of kinetic studies of reactions of this type (chiefly hydrogen and hydroxyl ion catalysis) have been used in an attempt to establish an experimental basis for the activity rate theory.[3] However, as already pointed out,[4] these experiments were carried out in solutions of high electrolyte concentration and are unsuitable for the purpose. In the first place, an investigation of the specific effect of the catalyst's activity cannot be carried out in concentrated salt solutions where numerous other factors influence the reaction rate and veil the effect sought. In the second place, one is prevented from taking advantage of the pronounced and uniform variations shown by ionic activity coefficients in dilute solution with change of salt concentration. For reactions studied in dilute solution the effect is linear and contradictory to the activity rate theory. A more critical test would be furnished by the study of a reaction involving a polyvalent ion, as in this case an exponential salt effect would be of much greater magnitude.

For these reasons a further experimental study of a reaction of the type

$$A^0 + B^z \longrightarrow \text{products}$$

where $z > 1$ in dilute solution seemed desirable. The reaction finally chosen was that between water and the hexa-urea chromium ion



$$6H_2O + Cr\left(CO\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right)_6^{+++} \longrightarrow Cr(H_2O)_6^{+++} + 6CO\Big\langle\begin{matrix}NH_2\\NH_2\end{matrix}$$

It is probable that the reaction takes place in steps and that the equation above does not represent the mechanism of the reaction. This, however, does not affect the kinetic equation

$$A^0 + B^{+++} \longrightarrow (A,B)^{+++} \longrightarrow \text{products}$$

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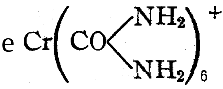
[3] (a) Harned, THIS JOURNAL, 40, 1461 (1918); (b) Harned and Pfanstiel, *ibid.*, 44, 2193 (1922); (c) Scatchard, *ibid.*, 43, 2387 (1921); (d) Fales and Morrell, *ibid.*, 44, 2071 (1922); (e) Åkerlöf, *ibid.*, 48, 3046 (1926); (f) Jones and Lewis, J. Chem. *Soc.*, 117, 1120 (1920); (g) Moran and Lewis, *ibid.*, 121, 1613 (1922).

[4] Brönsted, "Om Syre-og Basekatalyse" Københavns Universitet, September, 1926.

The reaction can be followed by determining the rate of disappearance of the



$Cr\left(CO\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}\right)_6^{+++}$

ion.

Experimental Part

The chromium urea chloride was prepared according to the method of **Pfeiffer**,[5] and converted to the nitrate by precipitation with nitric acid. Preliminary experiments showed that the reaction was very sensitive to diffused light. The rate of disappearance of the $Cr(NH_2CONH_2)_6^{+++}$ ion was determined by withdrawing samples of the reacting solution and precipitating with $K_3Co(CN)_6$ as $Cr(NH_2CONH_2)_6Co(CN)_6$. To test the quantitative accuracy of the method, known quantities of chromium urea nitrate were weighed out and the chromium urea cobalticyanide precipitated using varying excesses of potassium cobalticyanide and in the presence of different concentrations of potassium nitrate. The solubility of the precipitate increased in the presence of salt. Using a four-fold excess of potassium cobalticyanide (the filtrate being less than 0.01 molar in cobalticyanide) the method yielded results within 1% of the calculated weight in the presence of potassium nitrate up to 0.2 molar. Since the reaction is somewhat faster in pure water than in slightly acid solution, probably due to a slight effect of the OH ion, all experiments were carried out in solutions 0.001 *M* in nitric acid. The reaction is not catalyzed by hydrogen ion. The experiments were performed at 22.50° in a thermostat from which all light was excluded. A typical experiment ran as follows: 1.496 g. of chromium urea nitrate (0.002500 mole) was weighed out, dissolved in water, enough nitric acid was added to make the solution 0.001 M in nitric acid, and the whole was diluted to one liter and placed in the thermostat. At suitable intervals 100cc. portions were pipetted out and run into 15 cc. of solutions containing 0.001 mole of potassium cobalticyanide and enough potassium nitrate to make the final concentration of potassium nitrate 0.2 M. After cooling the solutions in ice, with frequent shaking, the precipitates were filtered onto weighed porous plate crucibles, washed with 5 cc. of water containing potassium cobalticyanide and finally with alcohol. The precipitates were dried at 90°.

The results are shown in Table I. The velocity constants are calculated by the formula

$$h = \frac{2.30}{t}\log_{10}\frac{c_0}{c_t}$$

where t is expressed in hours, c_0 represents the initial concentration and c^t that at time *t*.

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[5] Pfeiffer, *Ber.*, 38, 1926 (1903).

TABLE I

A TYPICAL EXPERIMENT

Time, hours	Wt. ppt., g. of $Cr(NH_2CONH_2)_6Co(CN)_6$		$k \times 10^5$
0	0.1575		...
46.3	.1154		672
71.9	.0961		687
120.1	.0691		681
144.1	.0602		668
168.2	.0509		669
102.1	.0434		671
		Average	674
		Av. dev.	0.9%

Table I shows that the disappearance of the chromium urea ion follows a unimolecular law. Table II gives a summary of the results of similar experiments carried out in the presence of potassium nitrate.

TABLE II

VELOCITY AT DIFFERENT SALT CONCENTRATIONS

$Cr(NH_2CONH_2)_6^{+++}$ 0.0025 M in all experiments; HNO_3 0.001 M

KNO_3, moles per liter	$k \times 10^5$	KNO_3, moles per liter	$k \times 10^5$
0	669	0 100	667
0.025	662	.150	G67
.050	674	.200	G58

From Table II it is evident that if there is any salt effect it is within the experimental error of the measurements (less than 2%). If the reaction rate were correctly expressed by the formula

$$V = k\, a_A a_B$$

the velocity constant would have decreased to approximately one-fourth its original value as the equivalent salt concentration increased from 0.0075 to 0.2075.[5a] My results are in direct contradiction to the activity rate theory and furnish substantial support to the Bronsted formula.

It is interesting to note that while the magnitude of the primary salt effect in this case is within the experimental error of the measurements, there are instances where the salt effect for this type of reaction is of considerable magnitude even in dilute solution. In the decomposition of nitrosotriacetonamine by hydroxyl ion the effect is about 7% in 0.1 N salt solution.[6,7] For the diazo-acetic ester reaction catalyzed by hydrogen ion the effect is 14% in 0.1 N salt solution.[8] For the mutarotation of glucose'the salt effect is again within the experimental error

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[5a] This estimate is based upon the change in the activity coefficient of a trivalent ion calculated from the solubility measurements of luteo hexacyano cobaltiate in potassium chloride solutions [Brönsted and Petersen, THIS JOURNAL, 43, 2265 (1921)].

[6] Bronsted and King, THIS JOURNAL, 47, 2523 (1925).

[7] Kilpatrick, *ibid.*, 48, 2091 (1926).

[8] Bronsted and Duus, *Z. physik. Chem.*, 117, 299 (1925).

of the measurements.[9] Other examples are given by Brönsted.[10] For hydrogen-ion catalysis the salt effect is positive and for hydroxyl-ion catalysis negative. In all cases the effect is linear in dilute solution and consequently cannot depend on the activity of the reacting ion.

The author wishes to thank Professor J. N. Bronsted for many valuable suggestions.

Summary

1. A kinetic study has been made of a zero type reaction in which the reacting ion is trivalent.

2. The reaction serves as a critical test of the activity rate theory and the Bronsted formula. The results are in agreement with the Brönsted formula.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE DIELECTRIC CONSTANTS OF BINARY MIXTURES. VI THE ELECTRIC MOMENTS OF CERTAIN NITRO DERIVATIVES OF BENZENE AND TOLUENE

BY JOHN WARREN WILLIAMS AND CHRISTIAN H. SCHWINGEL

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Measurements of the dielectric constants of binary mixtures in which the first component, the solvent, is known to have no electric moment permit a calculation of the molar polarization, and therefore of the electric moment, of the second component. This calculation has been detailed in a number of places.[1,2,3] The purpose of this paper is to present dielectric constant and density data for solutions of a number of nitro derivatives of benzene and toluene in the non-polar solvent benzene, with the results of the calculations for the electric moments of the solute molecules.

The method used for the determination of the dielectric constants of the binary mixtures was given in the first paper of the series.[4] Their densities were determined by means of an Ostwald-Sprengel pycnometer. Both dielectric constant and density determinations were made at 25°; in every case the usual precautions for precision work were taken.

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[9] Bronsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927).

[10] Bronsted, *Z. physik. Chem.*, 102, 169 (1922).

[1] Debye, "Handbuch der Radiologie" (Marx), 6, 597 (1925).

[2] Lange, *Z. Physik*, 33, 169 (1925).

[3] Williams and Krchma, THIS JOURNAL, 49, 1676 (1927).

[4] Williams and Krchma, *ibid.*, 48, 1888 (1926).

Purification of Materials

All substances used for the measurements reported were purified by the usual methods of crystallization or distillation or both. With the exception of the solvent, benzene, an outline of the method of purification for each particular substance used will not be given. These substances are tabulated with their melting points as determined by means of thermometers calibrated by the U. S. Bureau of Standards, and the method of purification used is indicated.

Benzene.—The benzene, obtained in a thiophene-free condition from the Eastman Kodak Company, was frozen out twice. After drying with phosphorus pentoxide it was fractionally distilled; boiling point (760 mm.) 80.10-80.20°.

Substituted Benzene Compounds

TABLE OF MELTING POINTS OF MATERIALS

Compound	Melting point, °C.	Compound	Melting point, °C.
Mononitrobenzene[a]	5.1– 5.4	*sym.*-Trinitrobenzene[b]	121.1–122.3
o-Dinitrobenzene[b]	116.0–116.5	o-Nitrotoluene[c]	–10.6––10.9
m-Dinitrobenzene[b]	89.0– 89.5	*m*-Nitrotoluene[c]	15.5– 16.0
p-Dinitrobenzene[b]	171.5–172.0	*p*-Nitrotoluene[b]	52.2– 52.9

[a] Purified by fractional crystallization and distillation.

[b] Purified by recrystallization from benzene.

[c] Purified by distillation.

Results

The results of the experimental determinations are given in Table I. The columns of this table give, from left to right, the mole fraction of the benzene which was used as the solvent, M. F. C_6H_6; the density of the solution, d_4^{25}; the observed dielectric constant, ϵ; the molar polarization of the solution, $P_{1,2} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{f_1M_1 + f_2M_2}{d} = f_1P_1 + f_2P_2$; and the molar polarization of the second component, $P_2 = \frac{P_{1,2} - f_1P_1}{f_2}$.

TABLE I

DIELECTRIC CONSTANT AND DENSITY DATA FOR MIXTURES

M. F. C_6H_6	d_4^{25}	ϵ	$P_{1,2}$	P_2
		Mononitrobenzene		
100.00	0.8731	2.283	26.74	348
96.88	.8850	2.98[a]	35.71	314
92.96	.9012	3.86	43.91	273
92.72	.9014	3.91	44.30	271
89.72	.9141	4.64	49.62	251
		o-Dinitrobenzene		
100.00	0.8731	2.283	26.74	800
99.63	.8761	2.48[a]	29.51	764
98.88	.8821	2.86	34.35	694
98.29	.8866	3.18	37.69	664
97.82	.8902	3.39	39.95	639

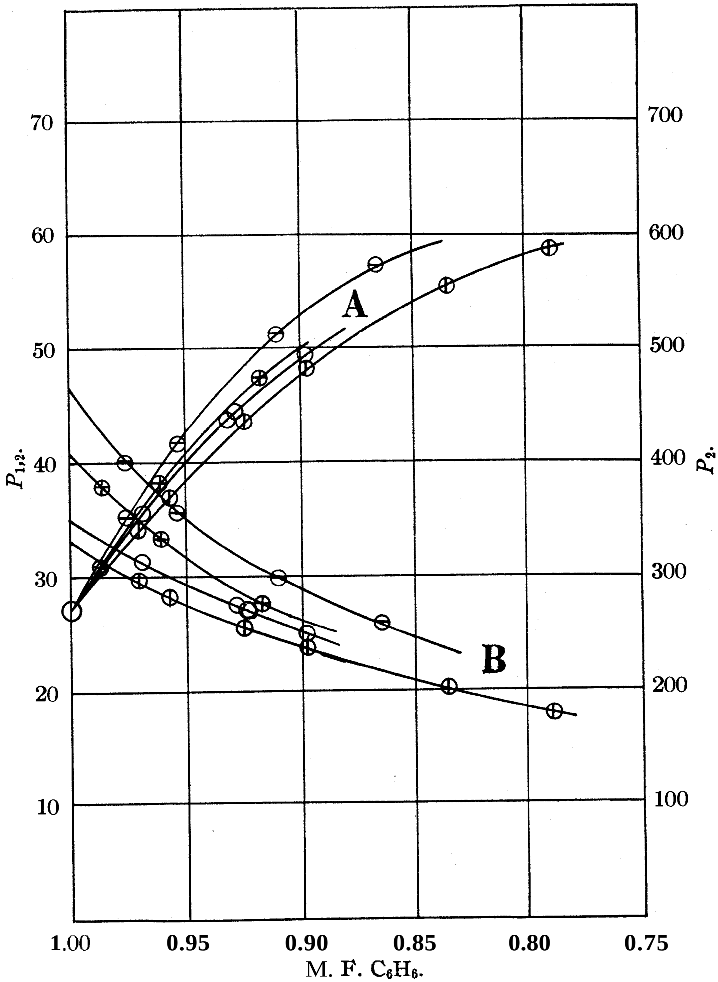
TABLE I *(Concluded)*

M. F. C_6H_6	d_4^{25}	ϵ	$P_{1,2}$	P_2
		m-Dinitrobenzene		
100.00	0.8731	2.283	26.74	338
98.46	.8852	2.60[a]	31.10	318
97.98	.8890	2.69	32.50	317
95.82	.9057	3.16	37.90	297
95.36	.9092	3.26	38.85	290
93.86	.9208	3.58	42.02	277
91.63	.9381	4.03	45.90	257
		p-Dinitrobenzene		
100.00	0.8731	2.283[b]	26.74	37.0
99.40	.8791	2.280	26.76	36.8
98.95	.8814	2.282	26.79	37.1
98.62	.8830	2.281	26.81	37.2
		sym.-Trinitrobenzene		
100.00	0.8731	2.283[b]	26.74	64.5
99.48	.8775	2.284	26.85	67.4
98.80	.8831	2.307	27.25	70.7
98.03	.8890	2.324	27.75	78.7
		o-Nitrotoluene		
100.00	0.8731	2.283	26.74	331
97.08	.8846	2.86[a]	34.45	297
95.80	.8892	3.08	37.21	284
92.46	.9022	3.77	43.70	254
89.50	.9135	4.36	48.70	237
83.50	.9284	5.34	55.70	203
78.80	.9492	6.20	58.80	179
		m-Nitrotoluene		
100.00	0.8731	2.283	26.74	407
98.74	.8782	2.62[a]	31.35	379
96.15	.8882	3.24	38.40	333
91.76	.9048	4.15	46.90	273
		p-Nitrotoluene		
100.00	0.8731	2.283	26.74	463
97.55	.8828	2.99[a]	35.80	400
95.38	.8911	3.58	41.87	355
90.93	.9082	4.77	51.15	298
86.52	.9248	5.88	57.60	257

[a] Correct to ±0.01.

[b] Correct to ±0.004.

In Fig. 1 are presented curves showing, first, the molar polarization of the solution plotted against the mole fraction of the solvent and, second, the molar polarization of the solute molecule plotted against the mole fraction of the solvent for mononitrobenzene and the nitrotoluenes. The latter curves are important in that they show exactly the manner in which the molar polarization of the second component, P_2, in infinitely dilute solution in the non-polar solvent is obtained. The molar polarization values of the second component for dilute solutions of finite concentration, obtained from the expression, $P_2 = (P_{1,2} - f_1P_1)/f_2$, are extrapolated to infinite dilution in the manner indicated. The curves for the other solute molecules are similar in all respects and have not been included.



⦶—*o*-Nitrotoluene, ⊕—*m*-nitrotoluene, ⊖—*p*-nitrotoluene, 0—mononitrobenzene; A—$P_{1,2}$ curves. B—P_2 curves.

Fig. 1.

Calculation of the Electric Moments of the Solute Molecules

The calculations of the electric moments of the various solute molecules were made in the manner described in a previous article,[3] and making like assumptions. The results of these calculations are given in Table II. The symbols used in the earlier article have been retained throughout.

TABLE II

ELECTRIC MOMENTS OF SOLUTE MOLECULES AT 25°

Molecule	P_a	P_2''	P_2'	$a \times 10^{18}$
Mononitrobenzene	348	33	315	3.90
o-Dinitrobenzene	800	35	765	6.05
m-Dinitrobenzene	338	35	303	3.81
p-Dinitrobenzene	37.0	35	2	0.32
sym.-Trinitrobenzene	64.5	40	24.5	1.08
o-Nitrotoluene	331	38	293	3.75
m-Nitrotoluene	407	38	369	4.20
p-Nitrotoluene	463	38	425	4.50

Discussion

The solute molecules were so chosen that the effect of the introduction of similar and dissimilar groups on the electric moment of the compound could be studied. Within the last two years data have accumulated so that the effect produced may be compared with the results of others. For example, Errera[5] has determined the electric moments of the various dichloro-, dibromo- and di-iodobenzenes, that is, benzene derivatives containing like atoms in various positions in the molecule. Smyth and Morgan[6] have also presented the results of experimental work and calculations for the dichlorobenzenes. Of the molecules studied in this article the dinitrobenzenes should show changes similar to those of the dichloro-, dibromo- or di-iodobenzenes. It is also possible to compare the results obtained for the nitrotoluenes, derivatives of benzene containing one positive and one negative group, with the calculations of Smyth and Morgan for the cresols.

For purposes of comparison Table III has been prepared. It is at once apparent that the changes produced in the electric moments of the molecules reported in this article parallel very closely the effects found by Smyth and Morgan,[6] not only in the case where similar atoms or groups of atoms are substituted in the benzene ring, but also in the case where dissimilar ones are substituted. And in the same manner that the moments of the various disubstituted compounds were calculated from vectorial considerations by these authors, it is possible to calculate the moments of the various dinitrobenzenes and nitrotoluenes, making use of the values $\mu = 3.90 \times 10^{-18}$ e.s.u. for nitrobenzene, and $\mu = 0.40 \times 10^{-18}$ e.s.u. for toluene.[7] The results of such calculations show an agreement with the experimentally determined values of the same order of magnitude

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[5] Errera, *Physik.* Z., 27, 764 (1926).

[6] Smyth and Morgan, THIS JOURNAL, 49, 1030 (1927).

[7] Krchma and Williams, *ibid.*, 49, 2408 (1927).

as that shown by Smyth and Morgan. In this connection an article by J. J. Thomson[8] is also of interest.

TABLE III

COMPARISON OF ELECTRIC MOMENT DATA

Smyth and Morgan		Williams and Schwingel	
Substance	$\mu \times 10^{18}$	Substance	$\mu \times 10^{18}$
C_6H_5Cl	1.61	$C_6H_5NO_2$	3.90
o-$C_6H_4Cl_2$	2.30	o-$C_6H_4(NO_2)_2$	6.05
m-$C_6H_4Cl_2$	1.55	m-$C_6H_4(NO_2)_2$	3.81
p-$C_6H_4Cl_2$	0	p-$C_6H_4(NO_2)_2$	0.32
C_6H_5OH[a]	1.73	$C_6H_5NO_2$	3.90
o-$CH_3C_6H_4OH$[a]	1.54	o-$CH_3C_6H_4NO_2$	3.75
m-$CH_3C_6H_4OH$[a]	1.76	m-$CH_3C_6H_4NO_2$	4.20
p-$CH_3C_6H_4OH$[a]	1.81	p-$CH_3C_6H_4NO_2$	4.50

[a] Calculated by Smith and Morgan from data of Philip and Haynes, *J. Chem. Soc.*, 87, 998 (1905).

The value of the moment found for symmetrical trinitrobenzene, $\mu = 1.08 \times 10^{-18}$ e.s.u., is, without doubt, too high. The same thing may be said of the value found for *p*-dinitrobenzene. From theoretical considerations zero values should have resulted. Owing to the limited solubility of these substances in benzene, the method of calculation becomes less accurate, so that the values obtained must be considered as being indistinguishable from zero.

Höjendahl, in a brief note to *Nature*,[9] has published the results of an experimental study in which the electric moments of a number of substituted benzene molecules are tabulated. In several cases a direct comparison between the results of Höjendahl and those of this article may be made. This comparison is given in Table IV.

TABLE IV

COMPARISON OF ELECTRIC MOMENT DATA

Molecule	$\mu \times 10^{18}$ (Williams and Schwingel)	$\mu \times 10^{18}$ (Höjendahl)
o-Dinitrobenzene	6.05	5.95
m-Dinitrobenzene	3.81	4.02
p-Dinitrobenzene	0.32	0.80
o-Nitrotoluene	3.75	3.62
p-Nitrotoluene	4.50	4.30

Since Hojendahl has taken the value $\mu = 3.75 \times 10^{-18}$ e.s.u. for the nitrobenzene molecule from the results of earlier work[1] and since the dielectric constant data were obtained with apparatus standardized using the data from which this value was calculated,[10] it would be expected that his results would be consistently lower than the ones reported in this

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[8] Thomson, *Phil.* Mag., 46, 513 (1923).

[9] Hojendahl, *Nature*, 117, 892 (1926).

[10] Conversation with Dr. Höjendahl

article, all of which are based on absolute measurements,[4] and which give a value, $\mu = 3.90 \times 10^{-18}$ e.s.u., for nitrobenzene in benzene solution. On this basis the results for o-dinitrobenzene and the nitrotoluenes must be virtually in agreement. In the case of the *p*-dinitrobenzene inaccuracies in the method of calculation which has to be employed will probably account for the high electric moment, $\mu = 0.80 \times 10^{-18}$ e.s.u., obtained by Höjendahl. Its value should approach zero.

The value obtained for m-dinitrobenzene, on the basis of the reasoning given above, is not in agreement with that reported in this article.

Höjendahl[10] has more recently repeated the measurements on the system benzene-m-dinitrobenzene, giving a value $\mu = 3.70 \times 10^{-18}$ for *m*-dinitrobenzene, one which is substantially in agreement with that presented in this article.

Summary

1. Dielectric constant and density data at 25° have been obtained for benzene solutions of nitrobenzene, o-, m- and p-dinitrobenzene, symmetrical trinitrobenzene and o-, m- and *p*-nitrotoluene.
2. The data have been applied to the calculations of the electric moments of the various solute molecules.
3. The results of these calculations have been critically discussed. In a number of cases they have been compared with the results of other investigators. They are in agreement with the physical basis provided by Errera, Smyth and Morgan, Thomson, and others, for the determination of the positive or negative character of the benzene substituents.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, PRINCETON UNIVERSITY]

A NEW METHOD FOR SEPARATING ARSENIC FROM ANTIMONY

BY LEROY W. MCCAY

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Introduction

The conversion of arsenic into arsenic acid according to Reich and Richter,[1] its precipitation as silver arsenate and the calculation of the arsenic from the weight of the salt, or the amount of silver in it, have been studied by Pearce and Low,[2] McCay[3] and, comparatively recently, by Eschweiler and Rohrs.[4]

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[1] Post, "Chemisch-Technische Analyse," Vieweg and Son, Braunschweig, 1881, p. 396; see also Dingler's *Polyt. Journ.*, 50, 475 (1883).

[2] Pearce and Low, *Chem. News*, 48, 85 (1883).

[3] McCay, *ibid.*, 48, 7 (1883); *Am. Chem. J.*, 8, 77 (1886).

[4] Eschweiler and Rohrs, *Z. angew. Chem.*, 36, 464 (1923).

When a *hydrofluoric* **acid** solution of arsenic acid is neutralized with ammonium or potassium hydroxide, and silver nitrate added to it, all of the arsenic is immediately precipitated as silver arsenate.

Antimonic acid and its alkali salts dissolve readily and completely in warm, moderately dilute hydrofluoric acid, and the solutions can be diluted indefinitely with water without becoming turbid. Such solutions yield no precipitates when neutralized or made alkaline with ammonium or potassium hydroxide. A neutral solution of an alkali antimoniate gives with silver nitrate a white, curdy precipitate of silver antimoniate. If, however, the solution be made strongly acid with hydrofluoric acid and then neutralized, the addition to it of silver nitrate forms no precipitate, if the materials and reagents are free from chlorides. The resulting solution is perfectly clear, and remains so permanently. Antimony pentafluoride is an extremely stable compound, so stable, indeed, that its aqueous solution, providing a little free hydrofluoric acid be present, undergoes no change, or a very sluggish one, when treated with hydrogen sulfide,[5] a fact used in testing antimonic acid for trivalent antimony. On the difference in the behavior of neutralized hydrofluoric acid solutions of arsenic and antimonic acids toward silver nitrate I have based a very satisfactory method for separating arsenic from antimony.

Experimental Part

A solution of dihydrogen potassium arsenate was made up by dissolving 12 g. of the salt in two liters of water, and the arsenic in 25 cc. was determined (1) by the pentasulfide[6] and (2) by the Reich-Richter method (Pearce-Low modification); found according to (1) 0.0631 and 0.0632 g. As, and according to (2) 0.0628 and 0.0630 g. The average of the four results is 0.0630 g. In a sample of crystalline potassium acid pyroantimonate tetrahydrate quite free from arsenic, the antimony was determined by dissolving a convenient amount in a small platinum dish in about 25 cc. of hot dilute nitric acid to which 2–3 cc. of 48% hydrofluoric acid had been added.[7] The solution was transferred to a 400cc. quartz dish, diluted somewhat, 10–15 cc. of concd. sulfuric acid was added to it, the liquid was evaporated as far as possible on the water-bath and then heated carefully[8] for a few minutes to strong fuming over a free flame. To reduce the antimony to the trivalent state, a piece of sulfur weighing

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[5] McCay, THIS JOURNAL, 31, 374 (1909); Furman, *Ind. Eng. Chem.*, 15, 1073 (1923), footnote.

[6] McCay, ***Am. Chem. J.*, *9*, *174*** (1887).

[7] Nitro-hydrofluoric acid is the best of solvents for tin and antimony and their alloys [McCay, THIS JOURNAL, 36, 2375 (1914)].

[8] Just before the acid begins to fume there is a slight effervescence, due probably to the decomposition of the fluorides. Owing to the size of the dish, however, there is little danger of loss.

about 2 g. was now dropped into the dish, it was covered and the acid heated to gentle boiling for twenty minutes. In the main

$$\mathrm{Sb_2O_5 + 2SO_2 = Sb_2O_3 + 2SO_3}$$

When cold, 100 cc. of dilute hydrochloric acid (20 cc. concd. HCl to 80 cc. of H_2O) was poured into the dish, the sulfur was filtered off, the volume of the filtrate brought to 200 cc. and the antimony determined with a 0.1 N $KMnO_4$ solution (Kessler),[9] or a 0.1 N $KBrO_3$ solution (Gyory).[10] Both solutions were standardized against purest antimony. The average of four closely agreeing results obtained by the former method was 47.95%, the average of two by the latter 47.96%. Of the two methods that of Gyory is the more reliable.

Weighed amounts of the pyro salt were dissolved as above directed in a platinum dish holding comfortably 250 cc., known volumes of the standard solution of the potassium arsenate run in, the volume in each case was brought to 100 cc. and the solution neutralized as follows: a drop of methyl orange was added and strong ammonia dropped in until every trace of pink had disappeared; the liquid was of a pure gold color and faintly but distinctly alkaline to sensitive litmus paper. The solution was then heated to boiling and the arsenic precipitated as silver arsenate with silver nitrate in slight excess. After long and vigorous stirring with a platinum spatula, tied to the end of a short stick, so as to coagulate the precipitate and cause it to settle completely, the clear supernatant liquid was tested with a piece of sensitive litmus paper. When not distinctly alkaline, a few drops of dilute ammonia (1 vol. concd. NH_4OH solution to 4 vols. H_2O) were added until the paper became decidedly blue and a single drop produced in the clear supernatant liquid no trace of turbidity. No precipitation of silver oxide is possible.[11] This method of neutralizing the solution is more reliable than that of Bennett.[12] His solutions contained no antimony and, of course, no hydrofluoric acid.

Silver arsenate is slightly soluble in water. According to G. S. Whitby,[13] 100 g. of water at 20° dissolves 0.00085 g. of the salt. According to my experiments, 100 g. of water at laboratory temperature dissolves 0.0013 g. (average of four well agreeing determinations). In water containing *silver nitrate*, even when ammonium nitrate or sulfate is present and the solution is decidedly ammoniacal, the solubility of the salt is practically negligible.

When cold, the silver arsenate was transferred to a filter paper, or Neubauer crucible, and washed with water containing ammonium nitrate

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[9] As modified by Petriccioli and Reuter, *Z. angew. Chem.*, 14, 1179 (1901).

[10] Gyory, Z. *anal. Chem.*, 32,415 (1893).

[11] Wetzlar, "Gmelin-Kraut's Handbuch der anorg. Chemie," 1914, Band V, **Abt.** 2, p. 68; Low, Chem. ***News*, 48,** 85 (1883).

[12] Bennett, THIS JOURNAL, 21, **431 (1899).**

[13] Whitby, *Z. anorg. Chem., 67, 107* (1910).

and a little silver nitrate (5. g. of NH_4NO_3 and 0.25 g. of $AgNO_3$ per liter). The amount of silver nitrate adhering to the well-drained precipitate is so small that it may be disregarded. For safety's sake, however, it may be removed with a little alcohol, the washings being rejected, as they contain no antimony. The precipitate was finally dissolved in nitric acid and the silver determined according to Volhard. The filtrate was caught in a Pyrex flask or beaker and, after the removal of the silver with a minimum amount of hydrochloric acid, poured into the large quartz dish, 10–15 cc. of concd. sulfuric acid was added and the evaporation, reduction and titration were carried out as already directed. Both arsenic and antimony being determined volumetrically, no errors can be caused by the entrance into the solutions of materials dissolved from the glass funnels, flasks, etc.

TABLE I

SEPARATION OF ARSENIC AND ANTIMONY

As taken (as H_2KAsO_4), g.	As found, g.	Antimony taken (as $H_2K_2Sb_2O_7 + 4H_2O$), g.	Antimony found, g.
0.0630	0.0630	0.1932	0.1933
.0630	.0629	.1514	.1516
.0630	.0628	.1201	.1205
.0630	.0630	.1105	.1104
.0630	.0631	.1404	.1405
.0252	.0251	.0960	.0958
.0252	.0252	.0965	.0973

The antimony was determined by titration with potassium permanganate.

While arsenic is converted into its higher state of oxidation with ease, the complete oxidation of antimony to its quinquivalent condition takes place with difficulty.[14] The product left on treating antimony with hot fuming nitric acid in large excess always contains some of the element in the trivalent condition. Concentrated hydrochloric acid and potassium chlorate, permanganic and chromic acids cannot for obvious reasons be employed here. My experience has been that potassium persulfate is the best reagent for effecting a complete oxidation. This fact having been established by a large number of qualitative experiments, 1.983 g. of pure antimony was dissolved in a platinum dish in 50 cc. of hot nitro-hydrofluoric acid, prepared by mixing 40 cc. of dilute nitric acid (1:4) with 5 cc. of 48% hydrofluoric acid. The resulting solution was diluted to about 100 cc., most of the free acid neutralized with ammonia, the liquid heated to gentle boiling and 6 g. of potassium persulfate added in small portions at a time. During the boiling the dish was kept covered with a quartz clock glass. When cold, the solution was neutralized with ammonia and diluted to 500 cc.; found, in 25 cc., 0.0994 g. of

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[14] Bošek, *Trans. Chem. Soc.*, 1895, p. 515; Hoffman, *Inaug. Dissert.*, Berlin, 1911.

Sb. By Rose's test[15] not a trace of trivalent antimony could be detected in it. With this standard solution[16] and that of the dihydrogen potassium arsenate used in the first series of separations the results given in Table II were obtained. To the mixture of convenient amounts of the two solutions a few drops of nitric acid and 2–3 cc. of hydrofluoric acid were added and the separations and determinations carried out as above directed.

TABLE II

SEPARATION OF ARSENIC AND ANTIMONY

As taken, g.	As found, g.	Sb taken, g.	Sb found, g.
0.0504	0.0507	0.0994	0.0993
.0504	.0508	.0994	.0993
.0252	.0253	.0994	.0996
.0126	.0124	.0994	.0994
.0126	.0126	.0994	.0997

The antimony was determined by titration with potassium bromate. Since dilute solutions of ammonium fluoride made slightly alkaline seem to have but slight action on Pyrex glass a number of separations were made in Pyrex beakers. The filtrates from the silver arsenate after removing the silver were evaporated in the large quartz dish. Although this dish has been used in a large number of determinations the inner surface still retains its highly pearly luster.

TABLE III

SEPARATION OF ARSENIC AND ANTIMONY IN PYREX GLASS

As taken, g.	As found, g.	Sb taken, g.	Sb found, g.
0.0630	0.0635	0.0994	0.0997
.0504	.0503	.0994	.0997
.0252	.0254	.0994	.0998

A mixture of 0.1026 g. of arsenious oxide and 0.1203 g. of potassium acid pyroantimonate tetrahydrate was dissolved and the arsenic and antimony were precipitated with hydrogen sulfide. The sulfides were treated in a platinum dish with fuming nitric acid, most of the acid was evaporated off, 2 cc. of hydrofluoric acid and a little water were added, the solution was warmed until clear and diluted to 100 cc. After oxidizing the antimony completely to the quinquivalent state with potassium persulfate, the separation of the two elements was made as directed: As taken (as As_2O_3) 0.0777 g.; As found, 0.0780 g.; Sb taken (as $H_2K_2Sb_2O_7 + 4H_2O$), 0.0577 g.; Sb found, 0.0579 g.

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[15] Fresenius, "Qualitative Chemical Analysis," John Wiley and Sons, Inc., New York, 1921.

[16] It was kept in a Pyrex flask. At the end of a month the liquid left was perfectly clear and the antimony concentration had not changed. A small, transparent, gelatinous deposit proved to be potassium silicofluoride.

If a mixture of the sulfides of arsenic, antimony and tin is to be examined, it is best dissolved in a small platinum or quartz dish in boiling concd. sulfuric acid, a piece of pure sulfur being dropped into the dish to yield sulfur dioxide which reduces the arsenic and antimony to the trivalent condition. After diluting the solution, adding hydrofluoric acid and filtering into a large platinum dish, the arsenic and antimony are reprecipitated with hydrogen sulfide and separated as above directed. The tin remains in solution and may be determined by any one of the methods proposed by McCay[17] and by Furman.[18] A mixture of the sulfides of arsenic, antimony and tin of known composition was analyzed: As taken, 0.0768 g.; As found, 0.0771 g.; Sb taken, 0.1208 g.; Sb found, 0.1215 g.; Sn taken, 0.2014 g.; Sn found, 0.2013 g.

Summary

1. From a hydrofluoric acid solution of arsenic and antimonic acids, made weakly but distinctly alkaline with ammonia, silver nitrate in excess precipitates completely the arsenic as silver arsenate, quite free from antimony.
2. The amount of arsenic is found by dissolving the precipitate in nitric acid and determining the silver in it by the method of Volhard.
3. The filtrate from the silver arsenate, after removing the silver with a minimum amount of hydrochloric acid, is mixed with concentrated sulfuric acid and evaporated, the acid heated to strong fuming, boiled gently in the presence of a piece of sulfur and the antimonous acid titrated with potassium permanganate or potassium bromate according to the details given.

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[17] McCay, THIS JOURNAL, 31, 373 (1909).

[18] Furman, *Ind. Eng. Chem.*, 15, 1071 (1923).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 159]

THE OXIDATION STATES OF RUTHENIUM IN ITS HALIDE COMPOUNDS

BY WILLIAM R. CROWELL AND DON M. YOST

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Introduction

In order to interpret the results of an investigation on the catalytic reduction of perchloric acid by hydrobromic acid,[1] and to make more complete the tables of reactions given in "Qualitative Analysis for the Rare Elements" by A. A. Noyes and W. C. Bray,[2] accurate information was needed as to the chemistry of ruthenium in its lower states of oxidation; for the literature on the nature and properties of the quadri-, tri- and bivalent compounds is not consistent. The experiments described in this paper were therefore carried out with the view of helping to remove the uncertainty as to the states of oxidation of ruthenium in its halide compounds.

We wish to express here our appreciation of the helpful suggestions made by Professor A. A. Noyes. Financial assistance was received through a grant made to him by the Carnegie Institution of Washington.

A review of the previous work has recently been published by J. L. Howe.[3] It will suffice therefore to mention here only those researches directly related to our investigation.

A series of experiments carried out by Ruff and Vidic[4] shows that ruthenium tetroxide is reduced completely by potassium iodide in normal acid to the trivalent state and no further; and that, when 2 N hydrobromic acid is used as the reducing agent, the reduction products consist of ruthenium in both the tri- and quadrivalent states, the proportions of each depending on the experimental conditions. Their results show, however, that even with hot concentrated hydrochloric acid trivalent ruthenium is produced only very slowly.

Under the belief that solutions of trivalent ruthenium chloride resulted from the action of hydrochloric acid, Remy and Wagner[5] obtained with sodium amalgam results which they interpreted as indicating that the deep blue compounds of ruthenium contain the metal in the univalent state, contrary to the prevailing idea that they are bivalent. Zintl and Zaimis[6] arrived at the same conclusion when they found that a small

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[1] These results are to be published in the near future.

[2] A. A. Noyes and W. C. Bray, "Qualitative Analysis for the Rare Elements," Macmillan Co., New York, 1927, p. 492.

[3] Howe, THIS JOURNAL, 49,2381 (1927).

[4] Ruff and Vidic, *Z. anorg. allgem. Chem.*, ***136***, 49 (1924).

[5] Remy and Wagner, ***Ber.***, 60, 493 (1927).

[6] Zintl and Zaimis, ***Ber.***, 60, ***842*** (1927).

excess over one equivalent of titanous sulfate or chromous sulfate produced a deep blue color in solutions which they believed to contain the ruthenium as a trivalent chloride. By reducing a ruthenium chloride and bromide dissolved in absolute alcohol with hydrogen in contact with platinum black, Gall and Lehmann[7] obtained deep blue solutions, from which on evaporation solid compounds resulted whose composition was found to correspond to the formulas $RuCl_2$ and $RuBr_2$. Zintl and Zaimis accounted for these compounds by assuming them to be $HRuCl_2$ and $HRuBr_2$; but the fact[8] that such compounds of other univalent metals are very unstable makes this assumption improbable.

Another source of confusion has arisen from the fact that until recently two distinct types of pentachlorosalts of trivalent ruthenium were believed to exist and were given the formulas $M_2RuCl_5.H_2O$ and $M_2Ru(H_2O)Cl_5$. Howe, however, as a result of the work of Charonnat[9] and recent experiments of his own, now considers that the formulas of these salts are $M_2RuCl_5.H_2O$ and M_2RuCl_5OH; that is to say, that the ruthenium in those compounds exists in the trivalent and quadrivalent states, respectively. It should be mentioned that S. G. C. Briggs[10] is not in aggreement with these conclusions.

Plan of the Investigation

The general plan of the investigation was as follows:

(1) To confirm the results of Ruff and Vidic that ruthenium is reduced by iodide in an acid solution to the trivalent state. This was done by determining the number of equivalents of iodine liberated in an acid solution of potassium iodide by the ruthenium tetroxide obtained by distilling with potassium permanganate a known volume of a stock solution of ruthenium chloride which had been evaporated with sulfuric acid to dense white fumes.

(2) To study the states of oxidation of ruthenium in the solution of its chloride obtained by dissolving in hydrochloric acid an hydroxide prepared by the reduction of potassium ruthenate with ethyl alcohol by the method of Krauss and Kiikenthal. This was done by determining the number of equivalents of iodine liberated in a hydrochloric acid solution of potassium iodide by known volumes of the ruthenium chloride solution before and after chlorination.

(3) To determine the states of oxidation of ruthenium produced by reduction of unchlorinated and chlorinated chloride solutions with titanous sulfate, especially its state in the yellow and deep blue solutions obtained successively with this reagent. This was done by making a potentiometric

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[7] Gall and Lehmann, *Ber.*, **59**, **2856** (**1926**).

[8] Engel, *Ann. chim. phys.*, [6] **17**, **378** (1889).

[9] Charonnat, *Compt. rend.*, **181**, **866** (**1925**).

[10] Briggs, THIS JOURNAL, **48**, **2127** (**1926**); *J. Chem. Soc.*, **127**, **1042** (**1925**).

titration of a known volume of the chloride solution with titanous sulfate, noting the number of equivalents of titanium required to produce a marked inflection in the titration curve and also the number of equivalents required to produce the yellow and blue colors in the solution.

(4) To study in ways similar to those described in (2) and (3) a salt of ruthenium bromide prepared by digesting the chloride with bromine and hydrobromic acid and evaporating the solution with potassium bromide.

Preparation of Standard Ruthenium Solutions

Stock solutions of ruthenium chloride were made by heating for five minutes just below the boiling point with concentrated hydrochloric acid an hydroxide which had been prepared by the reduction of potassium ruthenate with ethyl alcohol as described by Krauss and Kükenthal.[11] It was found that the hydroxide would not dissolve completely even on continued heating, but left a small black residue, which was filtered off. The concentration of the ruthenium was determined by evaporating definite volumes of the stock solution to dryness and igniting the residue in a stream of hydrogen, whereby the ruthenium is converted to the metallic state.

Reduction of Ruthenium Tetroxide by Iodide to the Trivalent State

Since the conclusion that ruthenium is reduced by iodide to the trivalent state is the basis of the following work, it seemed desirable to confirm the results of Ruff and Vidic to this effect. For this purpose a definite volume (5.00 cc.) of the stock solution of ruthenium chloride was evaporated with sulfuric acid till dense white fumes appeared; 10 cc. of water was added, followed by 20 cc. of a solution containing 1 g. of potassium permanganate, and the resulting mixtures were distilled in a current of carbon dioxide.[12] The distillate containing the ruthenium as tetroxide was absorbed in a 2 N hydrochloric acid solution containing potassium iodide. The liberated iodine was determined with standard thiosulfate. The results are given in Table I.

TABLE I

RESULTS OF THE DISTILLATION EXPERIMENTS

Cc. of Ru solution (0.01475 atomic)	Cc. of 0.0509 *N* thiosulfate Required	Cc. of 0.0509 *N* thiosulfate Calcd. for five equivalents	Atoms of iodine liberated per atom of Ru
5.00	7.10	7.25	4.90
5.00	7.24	7.25	4.99
5.00	7.17	7.25	4.95

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[11] Krauss and Kükenthal, *Z. anorg. allgem. Chem.*, 132, 316 (1924).

[12] This distillation process may also be used for the preparation of ruthenium tetroxide and is far more satisfactory for this purpose than any of the other known methods (see Ruff and Vidic, Ref. 4).

Reduction of Ruthenium by Iodide in Solutions of its Chloride

A definite volume (5.00 cc.) of a stock solution of ruthenium chloride 0.0295 atomic in ruthenium was diluted with enough water and hydrochloric acid to make the final acid concentration 2 N and the volume 100 cc.; 1 g. of potassium iodide was added and the liberated iodine was titrated with 0.0487 *N* thiosulfate, using starch as the indicator. Of the thiosulfate 0.76 cc. was used, while 3.03 cc. would have been required if the ruthenium had all been in the quadrivalent state. This shows that the ruthenium hydroxide prepared according to Krauss and Kükenthal contains a considerable proportion of quadrivalent ruthenium.

Chlorine was bubbled slowly for five minutes through two other 5.00-cc. portions of the stock solution in 100 cc. of 2 N hydrochloric acid, the excess of chlorine was expelled by boiling, 1 g of potassium iodide was added and the liberated iodine was determined as before.[13] Typical results are given in Table II.

TABLE II

IODIMETRIC TITRATION OF. RUTHENIUM CHLORIDE SOLUTIONS

Expt.	Cc. of Ru soln. (0.0295 atomic)	Cc. 0.0487 *N* $Na_2S_2O_3$ Unchlorinated soln.	Chlorinated soln.	Calcd. for one equivalent
1	5.00	0.76	..	3.03
2	5.00	..	3.02	3.03
3	5.00	..	3.10	3.03

The color of the unchlorinated solutions was light orange-red; that of the chlorinated solutions, dark orange-red.

These results show that in the chlorinated solution the ruthenium is all in the quadrivalent state, and that the acid solution of the hydroxide contains both trivalent and quadrivalent ruthenium.

Titration of Ruthenium Solutions with Titanous Sulfate

Measured volumes (5.00 cc.) of a stock solution 0.0148 atomic in ruthenium were diluted with enough water and hydrochloric acid to make the volume 50 cc. and the acid concentration 2 *N;* these solutions were titrated electrometrically in an atmosphere of carbon dioxide with a 0.0222 N titanous sulfate solution. The points where a rapid change in potential occurred are shown in Table III.

TABLE III

ELECTROMETRIC TITRATIONS OF RUTHENIUM SOLUTIONS WITH TITANOUS SULFATE

Expt.	Temp., C.	Cc. of Ru soln., 0.0148 atomic	Cc. of Ti^{III} soln., 0.0222 atomic Unchlorinated soln.	Chlorinated soln.	Calcd. for one equivalent
1	25	5.00	1.10	..	3.33
2	25	5.00	..	3.30	3.33
3	80	5.00	..	3.22	3.33

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[13] The possibility that RuO_4 might be present in the chlorinated mixtures is precluded by the concentration of the hydrochloric acid and the treatment by heating.

The electrometric titration curves corresponding to the experiments given in the table are shown in Fig. 1. A sharp break in the curves occurs when one equivalent of titanous salt is added to the chlorinated solution. In the case of the unchlorinated solution the break occurs when about one-third of an equivalent is added. No further breaks of a reproducible nature were observed in the curves, although several equivalents of titanous sulfate were always added.

The curves resulting from the titration of the cold mixtures are similar to that shown by Zintl and Zaimis. The color changes observed during the titration with titanous sulfate were practically the same as those described by them. At first the solutions are dark orange-red (if previously chlorinated). When nearly one equivalent of the reducing agent has been added the color becomes bright yellow. After passing the end-point the color changes rapidly through olive green to dark blue; and this blue color persists even after several equivalents have been added. In the solutions heated to 80° a small dark precipitate formed.

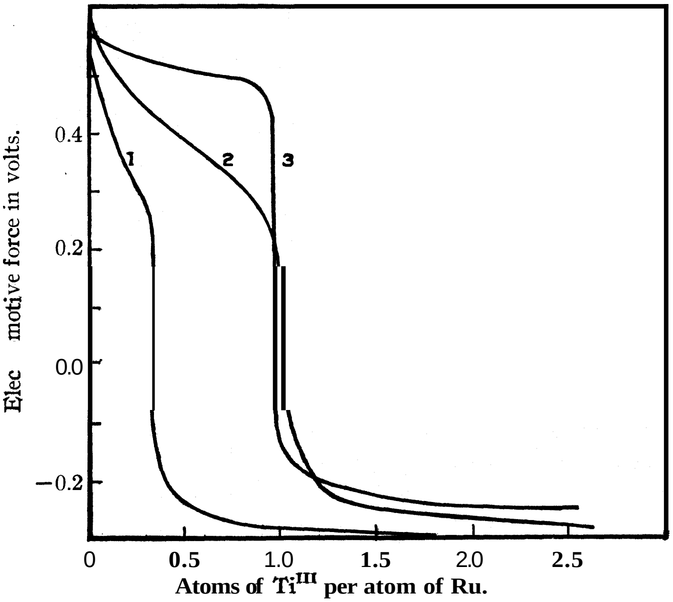

Fig. 1.—Electrometric titrations. Curve 1, unchlorinated solution at 25°; Curve 2, chlorinated solution at 25°; Curve 3, chlorinated solution at 80°.

These results clearly show that the sudden change in potential occurs when all of the quadrivalent ruthenium has been reduced, that is, at the transition from the trivalent to the bivalent state, and not at the transition from bivalent to univalent as concluded by Zintl and Zaimis, and that, therefore, in all probability, the blue color is characteristic of bivalent, not univalent, ruthenium as had been considered to be the case previous to the work of these investigators. In the case of the unchlorinated solution, the break in the curve confirms our conclusion, drawn from the iodimetric titrations, that quadrivalent ruthenium is present.

Preparation and Behavior of a Bromide Salt of Quadrivalent Ruthenium

It was found that when ruthenium chloride solutions containing moderate amounts of hydrobromic acid are heated with bromine a crimson solution results after the excess of bromine has been expelled. On treating these solutions with a small excess of potassium bromide and evaporating in a vacuum desiccator containing sulfuric acid and solid sodium hydroxide a black crystalline residue results. This residue was washed with water and alcohol and dried in the desiccator again. The product thus obtained was analyzed for bromine, potassium bromide and ruthenium as follows. A weighed amount was ignited in a stream of hydrogen, the hydrobromic acid liberated was absorbed in acidified silver nitrate solution and the resulting silver bromide dried and weighed. The potassium bromide remaining in the residue after ignition was extracted with water and the bromide in the extract was determined as silver bromide. Finally, the residue of ruthenium remaining after the extraction was ignited in a stream of hydrogen and then weighed as the metal. The salt was found to have the following percentage composition.

	Ru	KBr	Br (liberated as HBr)
Found, %	17.03	38 29	40 25
Calcd. for K_2RuBr_5OH, %	17 05	39 91	40 20

This is probably the same salt that Howe described originally[14] as $K_2RuBr_5.H_2O$, but which he now considers[3] to be K_2RuBr_5OH. The results given here are in accord with this conclusion but care must be exercised in drawing conclusions from the results of the analysis alone, for the calculated composition of the salt $K_2RuBr_5H_2O$ would also be in good agreement with the analytical results.

To determine to which of these formulas the behavior of the salt corresponds, its power of oxidizing iodide was studied. A solution of the salt was made up by dissolving a weighed amount in 2 N hydrochloric acid and diluting to a definite volume with more acid of the same concentration. Measured volumes of this solution were diluted to 100 cc. with 2 N hydrochloric acid, potassium iodide was added and the liberated iodine was titrated with standard thiosulfate. The results are presented in Table IV. They clearly show that in the bromide the ruthenium is in the quadrivalent state, thus eliminating the possibility that the salt is $K_2RuBr_5.H_2O$.

[14] Howe, THIS JOURNAL, 26, 944 (1904).

TABLE IV

IODIMETRIC TITRATIONS OF THE BROMIDE SALT

Expt.	Cc. of Ru soln., 0.00742 atomic	Cc. of 0.0500 *N* thiosulfate Used	Calcd. for one equivalent
1	10.00	1.40	1.48
2	20.00	2.95	2.96
3	25.00	3.65	3.70

Known volumes of the same stock solution were also titrated electrometrically with standard titanous sulfate solution, both before and after treating with chlorine. The excess of chlorine and liberated bromine was expelled by boiling. The color changes were the same as those observed in the experiments with the ruthenium chloride solutions. The results are recorded in Table V. They again show that in the bromide salt the ruthenium is quadrivalent.

TABLE V

ELECTROMETRIC TITRATIONS OF THE BROMIDE SALT

Expt.	Cc. of Ru soln., 0.00742, atomic	Cc. of Ti^{III} soln., 0.0280 atomic Unchlorinated soln.	Chlorinated soln.	Calcd.
1	10.00	2.65	..	2.65
2	10.00	2.62	..	2.65
3	10.00	..	2.70	2.65
4	10.00	..	2.70	2.65

Summary

The conclusion of Ruff and Vidic that ruthenium compounds in hydrochloric acid solution are reduced by iodide to the trivalent state and no further was confirmed by titrating with thiosulfate the iodine liberated in a solution of the tetroxide obtained by distilling with sulfuric acid and permanganate a known volume of a stock solution of ruthenium chloride which had been evaporated with sulfuric acid to dense white fumes (see Table I).

A hydrochloric acid solution of the ruthenium hydroxide prepared by reducing potassium ruthenate with ethyl alcohol by the method of Krauss and Kiikenthal was found to liberate about one-fourth of an atom of iodine per atom of ruthenium, showing that the hydroxide is a mixture of trivalent and quadrivalent compounds. When this solution was saturated with chlorine and the excess expelled by boiling, one atom of iodine was liberated for each atom of ruthenium (see Table II).

Electrometric titrations with titanous sulfate were made with the hydrochloric acid solution of ruthenium hydroxide and with the solution of it that had been treated with chlorine. In both cases an end-point was reached when all of the quadrivalent ruthenium had been reduced to the trivalent form, not as concluded by Zintl and Zaimis when the ruthenium was reduced to the bivalent state (see Table III and Fig. 1). It may therefore be concluded that the dark blue compounds which form after a small excess of titanous sulfate has been added are compounds of bivalent ruthenium, not of univalent ruthenium as supposed by these authors and by Remy and Wagner.

A bromide salt of ruthenium was prepared by digesting the chloride with bromine and hydrobromic acid and evaporating the solution with potassium bromide. An analysis of this salt showed that it conforms to the formula $K_2RuBr_5(H_2O)$ or K_2RuBr_5OH. Titrations of hydrochloric acid solutions of this salt with thiosulfate after treating it with potassium iodide, and with titanous sulfate by the electrometric method, showed that the ruthenium in the salt was in the quadrivalent state (see Tables IV and V). These results indicate that the true formula of the salt is K_2RuBr_5OH, thus confirming the recent views of Howe.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

THE CRYSTAL STRUCTURE OF THE SYSTEM CADMIUM-MERCURY

BY ROBERT FRANKLIN MEHL[1]

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The system cadmium-mercury is interesting for a number of reasons. Its composition-temperature diagram (Fig. 1) is the only known example of Roozeboom's Type IV.[2] Various compositions among the mercury-rich alloys have been used in the construction of standard cells. Numerous measurements on electrode potential, and on vapor pressure, of the liquid and partly liquid alloys have led a number of investigators to postulate the existence of intermetallic compounds.[3] These, however, do not appear on the constitution diagram proposed by Bijl[4] (Pig. 1) and repeatedly confirmed.[5] Recently T. W. Richards and C. E. Teeter, Jr.,[6] measured the heats of dilution of these alloys in mercury at room temperature and found no critical points suggestive of a compound.

A few measurements of the crystal structure of the system have been

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[1] National Research Fellow.

[2] Roozeboorn, Z. *physik. Chem.*, 30, 385 (1899).

[3] (a) Hildebrand, Foster and Beebe, THIS JOURNAL, 42, 545 (1920); (b) Richards and Forbes, *Carnegie Institution Publication,* No. 56 (1906); (c) Z. *physik. Chem., 58,* 738 (1906); (d) Hildebrand, *Trans. Am. Electrochem. Soc.*, 22, 319, 335 (1913).

[4] Bijl, Z. *physik. Chem.*, 41, 641 (1902).

[5] (a) Puschin, Z. *anorg. Chem.*, 36, 201 (1903); (b) Janecke, Z. *physik. Chem.*, 60, 409 (1907); (c) Schulze, *ibid.*, 105, 177 (1923); (d) Tammann and Mansuri, *Z. anorg. Chem.*, 132, 69 (1923).

[6] Unpublished research.

reported by Cl. v. Simson,[7] but apparently the study was only qualitative, for no analysis of structure was made.[8]

Although the structure of cadmium is well known,[9] the data for mercury are conflicting. L. W. McKeehan and P. P. Cioffi[10] studied its structure at the temperature of boiling liquid air and obtained diffraction spectra indicative of a simple rhombohedral structure, whereas N. Alsen and G. Aminoff[11] obtained diffraction data for mercury imbedded in solid carbon dioxide quite different, and concluded that at this temperature mercury is hexagonal. R. W. G. Wyckoff has briefly discussed these differences[12] and has suggested that the complete disagreement might be explained by the occurrence of a transition point.

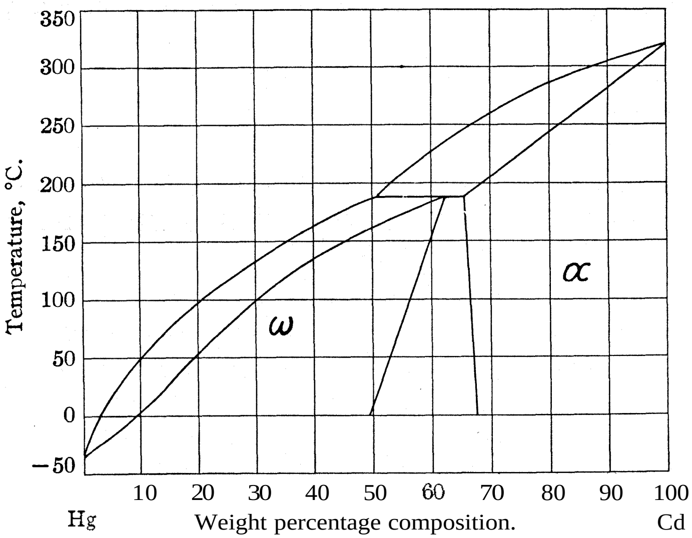

Fig. 1.

If we assume that the diagram of Bijl (Pig. 1) actually represents the mercury-cadmium equilibrium, the problem of the crystal structure af mercury can be attacked in an indirect way. Cadmium is the only metal, so far as known, which forms extensive solid solutions with mercury. Both the w- and the a-solid solution are terminal solid solutions, formed

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[7] Von Simson, *Z. physik. Chem.*, 109, 183 (1924).

[8] It is erroneously stated in this publication that the axial ratio of the pure, triangular close-packed cadmium is 1.39, whereas the true ratio is 1.89 (see the following reference).

[9] (a) Hull, *Phys. Rev.*, 17, 571 (1921); and others, (b) see International Critical Tables, Vol. I, p. 340.

[10] McKeehan and Cioffi, *Phys.* Rev., 19, 444 (1922).

[11] Alsen and Aminoff, *Geol. Fören. Förh.*, *44, 197* (1922).

[12] Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, p. 242.

presumably by simple substitution and exhibiting the space lattice of the solvent metal alone, possibly somewhat altered in dimension.[13] A determination of the structure of the ω-solid solution should, therefore, give the lattice type for mercury.

In order, therefore, to present additional evidence on the constitution of the cadmium-mercury system with especial reference to intermetallic compounds, and indirectly to determine the crystal structure of mercury (*with the assumption of the validity of the constitution diagram proposed by Bijl,*) the present study was undertaken.

Materials and Method

The alloys were made up determinately and not analyzed.[14] The cadmium bore a manufacturer's analysis of 99.961% cadmium, 0.015% zinc, 0.023% lead and 0.001% iron. The mercury was "Redistilled Mercury," which was passed through a nitric acid tower a dozen times and twice distilled in partial vacuum with a stream of dry air. The alloys were melted in Pyrex tubes under paraffin and quenched from the liquid state, the ω-solid solutions in liquid air and the α-solid solutions in ice water. No loss of mercury or cadmium was observed during the preparation and the synthetic compositions given in Table I are, therefore, to be taken as representative of the final compositions.

It became apparent soon after the beginning of the work that drastic deformation followed by prolonged annealing was necessary, especially for the ω-solid solution, to develop a structure crystalline enough to give sufficient diffraction lines for an analysis of structure. Each alloy bar (0.75cm. square) was therefore hammered on an anvil into a nail shaped piece, 0.30 cm. in diameter at the top, tapering to a point at the bottom. These pieces were annealed in a high temperature thermostat[15] and were subsequently treated as noted in Table I.

The powder method of analysis was used, with the "X-Ray Diffraction Apparatus" supplied by the General Electric Company. Early attempts to obtain spectra from wires were unsuccessful because of the high opacity of the alloys. Later experiments on alloy foil were abandoned when it was found an easy matter to obtain filings of the alloys sufficiently fine to pass a 200-mesh sieve. The powdered alloy mixed with finely ground

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[13] This is generally true of terminal solid solutions, with the exception of iron-carbon and manganese-carbon; see G. L. Clark, "Applied X-Rays," McGraw-Hill Book Company, New York, 1927, p. 204.

[14] Most of the alloys were stock alloys from another investigation (T. W. Richards and C. E. Teeter, Jr., unpublished research). The author wishes to thank Dr. C. E. Teeter, Jr., for his kindness in making them available for this work.

[15] Similar to that designed by J. H. Haughton and D. Hanson, *J. Inst. Metals,* No. *2,* 18, **173** (1917), except that the low temperature bulb was eliminated entirely. A constancy in temperature of 2 or 3 degrees up to 650 degrees was attainable.

TABLE I

TREATMENT OF ALLOYS

A = annealed; CD = cold drawn into wire; H = hammered; FSM = filed, sieved and mixed with flour.

Composition (weight % cadmium)	Treatment
23.0	H; A 48 hrs. 60°; FSM; A 72 hrs. 60–70°
27.3	H; A 36 hrs. 70°; CD; FSM; A 72 hrs. 70°
33.8	H; FSM; A 96 hrs. 100–104°
40.0	H; A 48 hrs. 120°; CD; A 72 hrs. 120°; FSM; A 72 hrs. 120°
47.1	H; A 72 hrs. 140"; CD; FSM; A 12 hrs. 140°
50.0	H; A 48 hrs. 150°; CD; FSM; A 12 hrs. 140°
60.1	H; A 48 hrs. 170°; FSM; A 72 hrs. 170°
73.0	H; A 48 hrs. 210°; FSM; A 48 hrs. 210°
80.0	H; A 48 hrs. 230°; CD; A 18 hrs. 225°; FSM; A 72 hrs. 220°
90.0	H; A 72 hrs. 260°; FSM; A 72 hrs. 260°
100.0	FSM

flour as a diluent,[16] and packed into thin-walled glass (Pyrex) tubes of inside diameter 0.5 mm. (approximately), gave the most satisfactory films. Half the length of each tube was devoted to the alloy powder, and the other half to a 1:1.7 mixture of twice recrystallized sodium chloride and flour.

Each film thus had the standard sodium chloride spectrum alongside the alloy spectrum. A film calibration was calculated from the measured positions of the sodium chloride lines[17] and applied to the lines measured for the alloy. All of the measurements given in Table II are so corrected. The time of exposure was usually twenty-four; hours, with 17–18 milliamperes passing through the X-ray tube.

Experimental Results

The measurements obtained from the films are given in Table II. The spectra obtained for the w-solid solution were much less sharp than those for the a-solid solution, and also less complete, as shown by Table II. Film 35 was probably the best in the ω-field. Film 36 was very poor, showing only scattered spots, with no fully developed lines. Film 40 was poor, with all lines diffused and striated except the one at 0.941° Å., which was sharp. Film 45 was poor.

It is clear from the data in Table II that the spectra for all compositions in the w-field are identical, not only in type but, within the error of measurement, in dimension also. Although the corresponding lines on the different films often appear to differ slightly in position, there is no progressive variation in position with alloy composition. In order to arrive at a series of values for the spectral lines best representative of the alloys

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[16] The table of dilutions proposed by W. P. Davey, *Gen. Elec. Rev.*, *28*, 589 (1925), was used in calculating the proportions of alloy powder and flour.

[17] Davey, Gen. *Elec. Rev.*, *29*, 121 (1926).

TABLE II

COMPOSITIONS IN WEIGHT PER CENT. OF CADMIUM

Composition of alloy	23.0		27.3	33.8	40.0		47.1	50.0		60.1		73.0		80.0	90.0		100.0
Film number	34	35	44	40	36	45	47	43	30	37	20	19	38	42	22	46	48
	2.80	2.79	2.81	2.81	2.82	2.80	2.78	2.77	2.77	2.85	2.83	2.81	2.83	2.81	2.81	2.81	2.82
	2.33	2.32	2.33	2.32	2.34	2.33	2.32	2.33	2.33	2.59	2.58	2.59	2.59	2.59	2.60	2.57	2.59
	1.977	1.970	1.97	1.99	2.01	1.98	1.961	1.96	1.96	2.35	2.34	2.33	2.35	2.34	2.36	(2.277?)	2.33
	1.498	1.498	1.502	1.512	...	1.501	1.483	1.492	1.494	1.915	1.904	1.895	1.910	1.894	1.91	1.90	1.892
	...	1.441	1.436	1.433	...	1.444	1.437	...	...	1.526	1.529	1.520	1.523	1.513	1.51	1.519	1.514
	...	1.389	...	...	...	1.384	...	...	...	1.480	1.486	1.485	1.481	1.482	1.485	1.490	1.485
	1.280	1.280	1.282	1.271	1.27	1.275	1.276	1.278	1.285	...	...	...	...	...	(1.400?)	...	(1.398?)
	...	1.241	...	...	...	...	...	...	1.235	1.316	1.316	1.314	1.316	...	1.313	1.316	1.308
	1.194	1.197	...	...	...	...	...	...	1.190	1.254	1.261	1.256	1.254	1.254	1.258	1.258	1.254
	1.162	1.162	1.159	1.153	1.158	...	1.164	1.160	1.160	...	...	...	(1.173?)	...	...	1.176	1.173
	1.020	1.020	1.028	...	...	...	...	...	...	1.060	1.068	1.058	1.058	1.060	1.057	1.062	1.059
	...	1.000	...	...	...	...	(1.000?)	...	...	1.028	...	1.026	...	1.027	1.026	...	1.024
	0.941	0.941	...	0.941	...	...	0.941	0.939	0.937	0.956	0.955	0.957	0.958	0.954	0.957	0.963	0.956
	...	.935	0.931	...	...	...	...	...	...	...	...	.862	.861	.861	.863	.862	.863
	...	.839	...	...	...	...	.850	.841	.844	...	...	.819	.821	.820	.820	.820	.821
	...	...	...	...	...	...	...	...	.773	...	...	...	...	.719	...	...	...
	...	...	...	...	...	...	...	...	...	...	...	...	...	.708	...	.709	...

investigated in the ω-field, the most sharply defined lines from the best films were averaged. These are given in Table III.

TABLE III

THE ω-SOLID SOLUTION

d **Average from** best films	Miller indices	*d* Theoretical **spacings**	Estimated intensities	Number of cooperating planes
2.785	100(2)	2.78	50	2
2.327	111	2.33	75	4
1.966	110(2)	1.965	12	2
1.495	131	1.500	42	8
1.438	001(2)	1.438	2	1
1.389	100(4)	1.390	3	2
1.281	101(2)	1.278	8	4
1.239	120(2)	1.239	trace	2
1.194	331	1.191	trace	4
1.161	111(2)	1.161	3	4
1.020	151	1.019	trace	8
1.000	201(2)	.994	trace	4
0.941	110(4)	.939	trace	2
...	121	934	1	8
(.844)	113		trace	4

The interplanar spacings observed correspond very closely to those required by either the face-centered tetragonal lattice of axial ratio 0.520 or the body-centered tetragonal lattice of axial ratio 0.740. These two lattices are equivalent and alternative.[18] Table III also gives the theoretical spacings as measured from the graph of Hull and Davey[19] for the face-centered tetragonal lattice of axial ratio 0.520. The intensities are averages taken from estimations on films numbers 42, 47, 44, **34,** 30 and **35.** The dimensions for the unit face-centered tetragonal prism are $a_0 = 5.570$ Å., $c_0 = 2.896$ Å., or for the unit body-centered tetragonal prism are $a_0 = 3.932$ Å., $c_0 = 2.910$ Å. The two values for c_0 should be equal. The difference originates in the error in the establishment of the correct axial ratios and in the absolute values of the lines chosen to give a_0.

The assumption of simple substitution in the ω-solid solution may be tested by a comparison of the calculated and the observed densities. Table IV gives the densities for a series of compositions calculated on the basis of a face-centered tetragonal lattice of axial ratio 0.520, which has four atoms in the unit cell. These densities are compared with densities obtained from the density-composition curve determined by Maey,[20]

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[18] An inspection of tetragonal symmetry shows that any face-centered tetragonal lattice is equivalent to a body-centered tetragonal lattice of axial ratio $\sqrt{2}$ times the axial ratio of the former.

[19] Hull and Davey, Phys. *Rev.,* 17, 569 (1921).

[20] Maey, *Z. physik. Chem.,* 50, 200 (1905).

and the agreement is found to be very good, indicating that the assumption of simple substitution is valid.

TABLE IV

DENSITY OF CADMIUM-MERCURY ALLOYS

Composition by weight, % cadmium	Calcd. density	Observed density (Maey)
0.0	14.72	(14.6–14.7)
23.0	12.48	12.43
30.0	11.93	11.96
40.0	11.21	11.25
50.0	10.58	10.72

The density for pure mercury calculated on the assumption of a face-centered tetragonal lattice of axial ratio **0.520** is **14.72.** It is interesting that an extrapolation on Maey's curve to the mercury axis indicates a density of solid mercury at room temperature between 14.6 and **14.7.** The atomic volume calculated from a density of **14.72** is **13.63,** as compared with **13.01** for pure cadmium. These atomic volumes are close, in conformity with the extensive solid solution formation observed. The density calculated from the data of McKeehan and Cioffi[21] for a temperature of —115° is **13.97,** and the corresponding atomic volume is **14.36.** If no solid-solid transitions are assumed, the effect of rising temperature should be to decrease the density and to increase the atomic volume. At room temperature, therefore, the density calculated from the data of McKeehan and Cioffi is much lower than that obtained by an extrapolation of Maey's density curve, and the atomic volume is much further from the atomic volume of cadmium than that calculated from the structure data on the ω-solid solution, a condition not favorable to the formation of extensive solid solution.

It seems possible, therefore, that the crystal structure of pure mercury at its melting point is the same as that observed for the mercury-rich cadmium-mercury solid solutions. If an actual determination of the crystal structure of mercury at its melting point should show a different lattice, the composition-temperature diagram of the system as proposed by Bijl would have to be modified. At present the weight of evidence seems to be against such a modification.

The 60.1% cadmium alloy comes in the heterogeneous field, $\alpha + \omega$, but shows only the lattice of the a-solid solution. The 73% cadmium alloy is in the a-field near the limit of solid solubility. No change in the lattice type or in the lattice dimensions are evident from the spectral lines given in Table I. A change in dimension would be manifested by a progressive change in the positions of the spectral lines with change in composition. No such displacement may be found in the measurements

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[21] Ref. **10, p. 445.**

given in Table II. The average positions of the various spectral lines calculated from films 19, 38, 42, 22 and 46 give a spectrum which agrees very closely with that obtained from film 48 for pure cadmium, both of which fit closely to Hull and Davey's graph for the triangular, close-packed lattice of axial ratio 1.89. The side of the unit triangle is 2.980 Å., as found by Hull.[9a] The density calculated for the 73% cadmium alloy is 9.72 as compared with the value 9.70 derived from Maey's data, indicating simple substitution in the a-solid solution.

There is no indication in the present work of the existence of any intermetallic compounds at room temperature. The composition range from 0 to 23% cadmium, however, has not been investigated, though if the structure of mercury at its melting point should prove to be similar to that observed for the ω-solid solution, the possibility for compound formation in this composition range would be very small. Nor does the present work afford any basis for the frequent postulation of intermetallic compounds in the liquid alloys, which if present in the liquid state should also be manifested in the solid state, since temperature rise usually has the effect of dissociation. So far as the author is aware there is no evidence of any intermetallic compound existent in the liquid state which is not also existent in the solid state.[22]

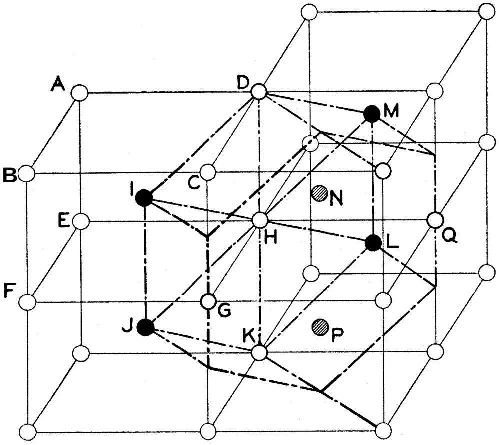

Fig. 2.

Although the similar atomic volumes of mercury and cadmium doubtless favor the extensive solid solution formation observed, it is difficult to see why two lattices so different as the face-centered tetragonal and the close-packed triangular should show such an extensive isomorphism. The tetragonal lattices pictured in the usual way, with lines drawn parallel to the tetragonal coordinates, do not suggest the presence of any hexagonal arrangement of atoms. It should be distinctly emphasized, however, that these lines are purely artificial, and that important orientations exist in many lattices which they are insufficient to depict and in fact frequently mask.

It may be shown, however, that in the w-solid solution there is actually an hexagonal arrangement closely approximating the unit hexagonal

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[22] **Cf. the work of Bornemann, et al., on the electrical conductivity of liquid alloys,** *Metallurgie,* **7,396,655,730,755 (1910); 9,473 (1912);** *Ferrum,* **11,276,289,330 (1913)**

prism in the a-solid solution. Fig. 2 represents six unit cells of the body-centered tetragonal lattice exhibited by the o-solid solution. Cell ABCD-EFGH is such a unit cell. Let us consider, however, atoms DIJKLM, which lie in a plane and form a hexagon. Geometrically it may be shown that for the lattice of the ω-solid solution DI = DM = JK = KI, = 3.139 Å., and that IJ = MI, = 2.910 Å.; angle IDM = angle JKI, = 125°46′, and angle DMI, = angle MLK = angle KJI = angle JID = 117'7'. This hexagon is therefore nearly equilateral. It may also be shown that it is the basal hexagon of an hexagonal prism, half of which is indicated in Fig. 2 by dotted lines. Fig. 3 represents the fully developed prism. The similarity between this and the ordinary close-packed hexagonal prism is striking, and would be complete if DIJKLM were a perfect hexagon and if atoms G, N, Q and P were displaced to the left in their plane so that atom P were brought into the center of the triangular prism of which JKH is a basal plane. The same is true of the other atoms in the GNQP plane. This deformed hexagonal prism is repeated throughout the lattice and serves completely to define it, that is, it is a unit cell. The density for the 40% cadmium alloy calculated from it agrees with that given in Table IV. The basal hexagon will be equilateral when the axial ratio for the body-centered tetragonal lattice is 0.816.

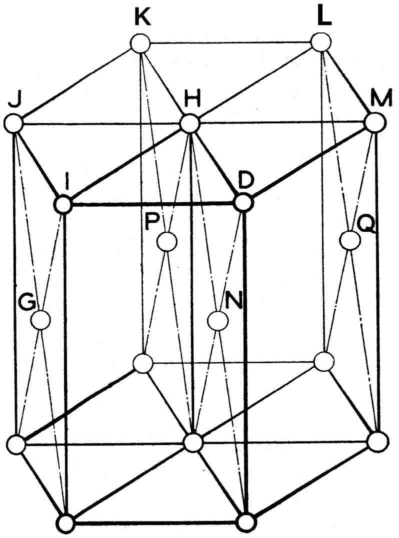

Fig. 3.

The dimensions of the unit cell are $a_0 = 3.139$ Å., $a_0' = 2.910$ Å., $c_0 = 5.561$ Å., whereas the dimensions of the unit hexagonal cadmium prism are $a_0 = 2.980$ Å. and $c_0 = 5.632$ Å. The a- and the ω-solid solutions are therefore very similar both in lattice dimensions and in atomic volume, thus satisfying two of the conditions necessary for solid solutions formation.

The author wishes to acknowledge his indebtedness to Professor Albert Sauveur, whose kindness made available the apparatus used in this work.

Summary

The crystal structure of the system cadmium-mercury has been investigated by a study of the diffraction of X-rays. It has been shown that there are at least two, and probably only two, types of lattice in the system, a face-centered tetragonal lattice of axial ratio 0.520 (or a body-centered lattice of axial ratio 0.740) found in alloys of from 23 to 50%

cadmium by weight, and a triangular close-packed lattice of axial ratio 1.89, found in alloys of from 60 to 100% cadmium by weight.

The conflicting data on the crystal structure of mercury are discussed and it is suggested that the present work indirectly indicates a face-centered (or body-centered) tetragonal structure. It is pointed out that the frequent assumption of intermetallic compounds in this system receives no support from the present crystal structure data.

The isomorphism of cadmium and the face-centered tetragonal component (which may be mercury) is favored by similar atomic volumes and also by the presence in the face-centered tetragonal lattice of an atom arrangement closely approximating the unit hexagonal prism of cadmium both in lattice type and in the unit cell dimensions.

[CONTRIBUTION FROM THE KAISER WILHELM-INSTITUT FÜR PHYSIKALISCHE CHEMIE UND ELEKTROCHEMIE]

A NEW METHOD FOR THE STUDY OF CATAPHORETIC PROTEIN MOBILITY[1]

BY HAROLD A. ABRAMSON

RECEIVED NOVEMBER 19, 1927 PUBLISHED FEBRUARY 4, 1928

It has previously been shown[2] that the cataphoretic migration of inert particles suspended in gelatin gels represents the movements of the micellae of the gelatin. That is, there seemed to be a rapid formation of a sheath of the gel about the particle which changed its sign at the iso-electric point of the protein. The study of the migration of the particle, therefore, afforded a simple means of studying the cataphoresis of the gelatin micellae themselves. This has led to the study of the influence of proteins on the migration of quartz particles in sols of low concentration. A concentration of 1 X 10^{-7} already lowers ζ, the electrokinetic potential, appreciably. Between concentrations of about 1.10^{-5} and 1.10^{-4} g. per liter the maximum effect of the protein is reached and the particles behave like gelatin. Egg albumin shows a similar influence.

A suspension of quartz particles in a dilute solution of the proteins mentioned (within limits of dilution) gives the absolute electrophoretic migration of the protein micellae. The complete data and theory of these phenomena will be presented elsewhere.[3] Svedberg and Tiselius[4] have used a rather elaborate method to determine the mobility of egg albumin. It seemed that a comparison of their method with ours was of interest.

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[1] The researches here reported were made in part during a tenure of a Medical Fellowship of the National Research Council.

[2] Freundlich and Abramson, Z. *physik. Chern.*, 128, 25 (1927).

[3] Z. *physik. Chern.*, in press.

[4] Svedberg and Tiselius, THIS JOURNAL, 48, 2272 (1926).

Method

The migration of the quartz particles was studied in a type of micro-electrophoresis cell described elsewhere.[2] Fairly pure powdered egg albumin (Merck) is made up in $M/50$ acetate buffer solutions.[5] Concentrations of 1×10^3 g. per liter of egg albumin are preferred because at this concentration the correction for dielectric constant is probably negligible and the solutions are sufficiently concentrated to give maximum values of {. The quartz particles should be between 0.5 to 5.0μ, and 1.0 mm.^{3} of the final solution should have between 10,000 to 100,000 particles. No attention need be paid to the shape or state of aggregation of the quartz particles as, contrary to the theoretical considerations of Debye and Hückel,[6,2] cataphoretic migration of quartz particles in water and aqueous solutions is independent of the form of the particle and of the state of aggregation. Consequently, measurements may be made from any particle. (An occasional particle shows a wide deviation from the mean which is unexplainable on the basis of its shape. Such values are discarded.) Although equilibrium seems to set in more quickly, fifteen minutes are allowed to elapse between the making of the suspension and the measurements.

Experimental

The data for egg albumin are presented here in order to compare our values with those of Svedberg and Tiselius for the same protein.[4] These authors used a 1.0% albumin solution. As the dielectric constant of a solution of this protein at this concentration is 72,[7] it follows from the Helmholtz-Lamb equation, $V = \zeta HD/4\pi\eta$, in which V = velocity of particle, ζ = electrokinetic potential, H = potential drop per cm., η = viscosity of the medium, all in C. G. S. electrostatic units, that the values observed by Svedberg and Tiselius in the more concentrated solution should be lower than those observed here. Further, the presence of a 1% protein solution may alter the {-potential itself (see Table II). This is actually the case. The data given in Table I, a typical experiment, have been

TABLE I

TYPICAL EXPERIMENT

PH	μ/sec./volt, cm.	ζ-pot., mv.	PH	μ/sec./volt, cm.	ζ-pot., mv.
3.4	+2.1	+27	4.8	Negative	Negative
3.9	1.6	21	5.0	−0.35	−4.5
4.2	0.8'3	11	5.3	.57	7
4.4	.55	7	5.55	− .68	−8
4.65	+ .30	+ 4			

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[5] International Critical Tables, Vol. 1, 84 (1926).

[6] Debye and Hückel, Physik. Z., 25, 49 (1924); Hiickel, ibid., 25, 704 (1924).

[7] Fiirth, Ann. Physik. 70, 60 (1923).

obtained from a 1.10^{-3} g. per liter egg albumin solution. The ζ-potential has been calculated using the values given for water of D and η.

TABLE II

DATA RECALCULATED PROM SVEDBERG AND TISELIUS

*P*H	μ/sec./volt, cm.	ζ-pot., mv.	*P*H	μ/sec./volt, cm.	ζ-pot., mv.
3 4	$1.7	+22	5 0	0.40	5
3.96	0.92	12	5.25	.58	7.5
4.27	.31	4	5.36	.11	10
4.5	+ .16	+ 2	5.75	−1.0	−13
4.81	− .09	− 1.5			

In Pig. 1, Svedberg and Tiselius' data have been corrected for D, and have been also recalculated for 21°. The dots represent our data from three different experiments. The open circles are the recalculated figures

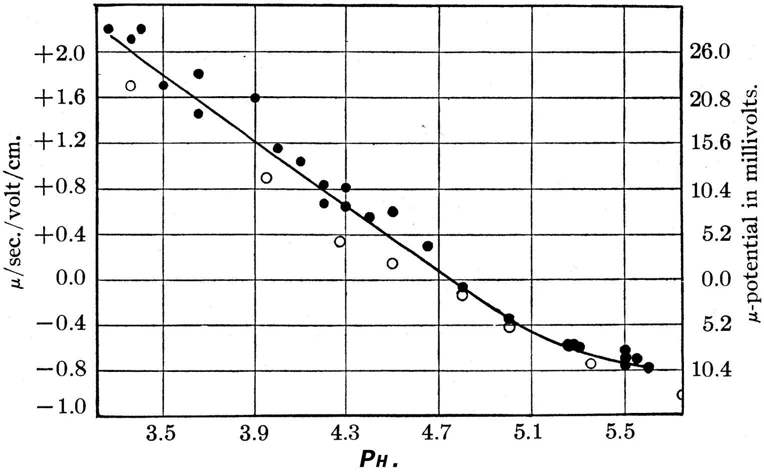

Fig. 1.—The dots indicate protein mobility found in the experiments described in this communication. The open circles are the recalculated data from Svedberg and Tiselius. The signs on the ordinate refer to the charge.

of Svedberg and Tiselius. This correction is 15% for the difference in temperatures and 11% for D. It is evident that the method presented here compares favorably with that of Svedberg and Tiselius. It is further obvious that it affords a most sensitive means of detecting proteins in extremely small quantities and presents a new means of studying their behavior. It also admits of a macroscopic variation.

It is a pleasure to thank Professor H. Freundlich for his continued guidance.

Summary

1. Quartz particles suspended in dilute protein solutions under certain

conditions move cataphoretically as if the migration were due to a surface consisting of the pure protein.

2. Based upon this adsorption of protein by quartz, a method for studying the mobility of protein is presented.

3. The results for egg albumin for a variable hydrogen-ion concentration agree satisfactorily with the values given by Svedberg and Tiselius.

BERLIN-DAHLEM, GERMANY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, THE UNIVERSITY OF MINNESOTA]

THE DETECTION OF TRACES OF BERYLLIUM AND THE COLORIMETRIC DETERMINATION OF THIS ELEMENT

BY I. M. KOLTHOFF

RECEIVED NOVEMBER 21, 1927 PUBLISHED FEBRUARY 4, 1928

Recently[1] it has been shown that adsorption indicators can be used advantageously for the detection and colorimetric determination of some elements. In a solution weakly acid with acetic acid and acetate (PH about 5.5) aluminum, for example, gives a very nice and sensitive color reaction with 1,2,5,8-oxyanthraquinone. For magnesium, we found titan yellow to be an excellent reagent.[2]

In investigations on the solubility of the slightly soluble metal hydroxides it is of great practical advantage to have color reactions at our disposal with which we can determine traces of dissolved oxides. For the determination of the solubility of beryllium hydroxide (which is extremely small at the isoelectric point) at different hydrogen-ion concentrations we wanted such a method. As is well known, there are only a very few characteristic reactions for beryllium, and only two color reactions have been described in the literature.[3] For this reason we tried to detect and determine it by means of adsorption indicators. The beryllium hydroxide is precipitated at the proper PH in the presence of some useful indicator and the color of the solution or the lake formed is observed.

1,2,5,8-Oxyanthraquinone as Indicator[4] (0.1% solution in alcohol).—To 10 cc. of the solution, 0.1cc. indicator and 6 to 8 drops of 4 *N* ammonia

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[1] Kolthoff, *Chem. Weekblad,* 24, 447 (1927).

[2] Kolthoff, *ibid.,* 24, 254 (1927).

[3] The aluminon (aurintricarboxylic acid), which forms a red lake with aluminum [Hammett and Sottery, THIS JOURNAL, 47, 142 (1925); Lundell and Knowles, *Ind. Eng. Chem.,* 18, 60 (1926)], is also suitable for the detection of beryllium [A. R. Middleton, THIS JOURNAL, 48, 2125 (1926)]. According to the statements of Middleton, this reaction is not as sensitive as those described below in this paper.

[4] After writing this paper the author found that the reagent has been already applied by Hellmut Fischer, *Wissenschaftl. Veröffentl. Siemens Konzern,* 5, 99 (1926); *Chem. Zent.,* 1927, *I,* 495, who determined the dyestuff in the lake in a colorimetric way. As no details are given in the abstract referred to, the practical statements made above may be of some value.

are added, the mixture is boiled and the color observed after five minutes' standing.

A solution containing 500 mg. of beryllium in a liter gives a flock with dark blue color; the supernatant liquid is colorless. With 50 mg. of beryllium per liter, the lake is violet blue; with 5 mg. of beryllium per liter no lake is formed; the solution has a blue-violet color.

A blank without beryllium gives a violet color; if the color of the unknown is compared with that of the blank, 0.5 mg. of beryllium per liter may be detected by the blue-violet color.

In the presence of ammonium chloride, the sensitivity is not changed, the lake formed settling out much sooner. Ten cc. of solution with 0.1 cc. of indicator, 1 cc. of 4 N ammonium chloride and 6 to 8 drops of 4 N ammonia are boiled and observed after five minutes. Five mg. of beryllium per liter gives a flock with a blue-violet color. More dilute solutions only give a blue-violet color (as without ammonium chloride); after standing overnight the lake flocculates with the same shade. In this way even 0.5 mg. of beryllium per liter can be detected. Aluminum, which very often occurs in the presence of beryllium, interferes. It forms a violet lake with the dyestuff and in the presence of excess aluminum the blue-violet color of the beryllium lake can no longer be seen. The aluminum has to be removed (see below)

Unfortunately, the blank without beryllium gives a solution with a violet color, and for this reason it is hard to apply the reaction described for a colorimetric determination of the element. Therefore a search was made for some other reagent more suitable for this purpose.

Curcumin as Reagent (0.1% solution in alcohol).—In weakly alkaline solution, this indicator is adsorbed by the beryllium hydroxide with the formation of an orange-red color.

To 10 cc. of solution are added 1 drop of indicator (no more), 0.5 cc. of 4 N ammonium chloride and 6 to 8 drops of 4 N ammonia.

A solution containing 50 mg. of beryllium per liter gives a flocculent precipitate with a red color; with 1 mg. of beryllium per liter the color is orange-red. If the color is compared with that of a blank, the sensitivity may be increased to 0.05 mg. of beryllium per liter. The color of the blank is yellow-brown.

The appearance of the solution changes on standing, as the lake flocculates. After standing overnight, the adsorption compound sinks to the bottom of the test-tube and may be detected by its color (orange-red).

The reaction is very suitable for the quantitative colorimetric determination of beryllium in concentrations between 1 and 0.05 mg. per liter. If the color is compared with solutions of known beryllium content after the same time of standing, the method gives good results. Not more than

0.5 to 1 cc. of 4 N ammonium chloride should be added to 10 cc. of solutions; otherwise the sensitivity is decreased.

Potassium, sodium, lithium, calcium and barium do not interfere. Magnesium decreases the sensitivity somewhat, but 1 mg. of beryllium per liter in the presence of 1 g. of magnesium per liter can be detected in the way described.

Aluminum has a disturbing effect as it also forms a colored lake. For the detection of aluminum this reaction, however, is not very suitable. If beryllium is to be detected in the presence of aluminum, the slightly acid solution is treated with an excess of sodium fluoride. The main part of aluminum precipitates in the form of Na_3AlF_6, and the rest in solution does not interfere. After standing for one hour, the liquid is filtered and the filtrate treated in the way described above. One mg. of beryllium per liter could be detected in the presence of 1 g. of aluminum per liter. We may remark here that sodium fluoride decreases the sensitivity of the reaction for beryllium somewhat.

Ferric iron interferes and can be made harmless in the same way as described for aluminum. Or, more easily still, the iron may be precipitated at room temperature with an excess of sodium hydroxide, and 1 drop of curcumin and an excess of ammonium chloride added to the filtrate. Two mg. of beryllium per liter in the presence of 1 g. of iron per liter could be easily seen.

It may be mentioned here that in strong alkaline solutions beryllium does not react with the curcumin (the beryllium hydroxide dissolves again). Under these conditions magnesium gives a distinct color reaction, however, not as sensitive as with titan yellow.

Ten cc. of solution with 1 drop of reagent and 1 cc. of 4 N sodium hydroxide gives an orange color with 10 mg. of magnesium per liter, an orange-yellow color with 5 mg. per liter and an orange-brown color (distinctly different from a blank) with 1 mg. per liter. Perhaps the curcumin is useful for determining amounts of magnesium between 1 and 10 mg. of magnesium per liter.

The tap water of Minneapolis, containing 16.5 mg. of magnesium per liter, gave a very distinct reaction.

Summary

1. Curcumin is a very useful reagent for the detection and colorimetric determination of traces of beryllium.

2. The sensitivity extends to 0.05 mg. of beryllium per liter.

3. A method is described for the detection of beryllium in the presence of aluminum and ferric iron.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE PORTLAND CEMENT ASSOCIATION FELLOWSHIP, BUREAU OF STANDARDS]

STUDIES ON THE SYSTEM CALCIUM OXIDE-ALUMINA-FERRIC OXIDE[1]

BY W. C. HANSEN, L. T. BROWNMILLER AND R. H. BOGUE

RECEIVED NOVEMBER 25, 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

This investigation of the system calcium oxide-alumina-ferric oxide has been undertaken as one step in a program to determine the constitution of portland cement and the role played by each component in the manufacture and utilization of cement. The system has been found to be complex and only that part has been explored which appears to be of significance in the above-mentioned problem. This part, however, includes a large portion of the system.

Very little pertaining to the system CaO-Al_2O_3-Fe_2O_3 is found in the literature. Three contributions have been made, however, which are of interest.

Le Chatelier[2] believed that a compound existed of the composition $3CaO.Al_2O_3.Fe_2O_3$.

Shepherd, Rankin and Wright[3] observed that $2CaO.Fe_2O_3$ and $5CaO.3Al_2O_3$ reacted, but the reaction products were not determined.

Campbell[4] found that alumina and ferric oxide were capable of replacing each other in certain combinations with calcium oxide.

The Binary Systems

Two of the binary systems making up the ternary system under consideration have been studied. These are the systems CaO-Al_2O_3[5] and CaO-Fe_2O_3.[6] The system Al_2O_3-Fe_2O_3 has not been reported but a knowledge of it is not necessary for the investigation given here.

The data from these systems are plotted[7] on the sides of the triangular diagram, Fig. 1. Dotted lines have been drawn out from the quadruple points to indicate the origin of the boundary curves. With this preliminary information we are in a position to determine the ternary combinations and temperature relations existing in a part of the ternary system

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[1] Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce. Paper No. 13 of the Portland Cement Association Fellowship at the Bureau of Standards.

[2] Le Chatelier, *Compt. rend.*, *94*, 13 (1882).

[3] Shepherd, Rankin and Wright, *J. Ind. Eng. Chem.*, 3, 211 (1911).

[4] Campbell, *J. Ind. Eng. Chem.*, *11*, 116 (1919).

[5] Rankin and Wright, *Am. J. Sci.*, *39*, 11 (1915).

[6] Sosman and Merwin, *J. Wash. Acad. Sci.*, *6*, 532 (1916).

[7] Abbreviated formulas are used in Fig. 5 to conserve space. These are as follows $C = CaO$; $A = Al_2O_3$; $F = Fe_2O_3$.

and the stability fields for calcium oxide and some of the binary and ternary compounds.

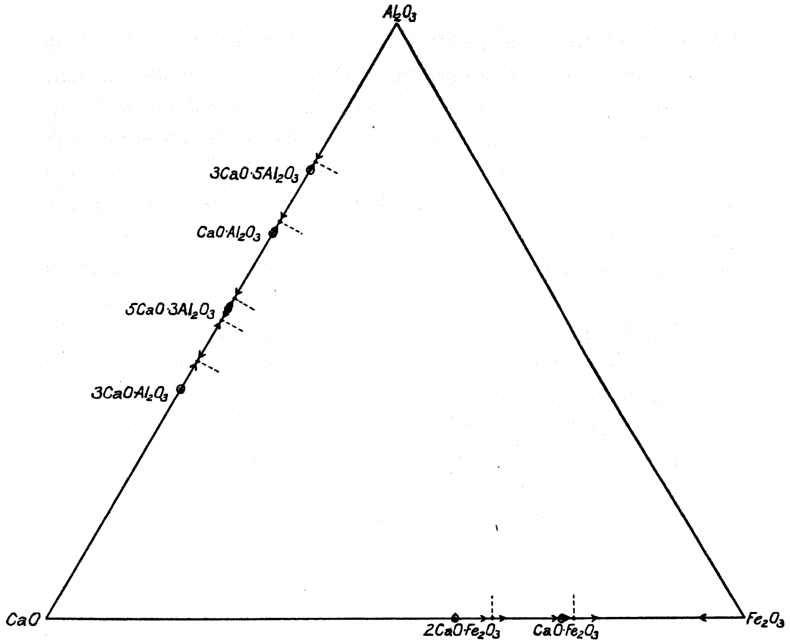

Fig. 1.—Compositions of the binary compounds and quadruple points projected on the ternary diagram.

The Ternary System

Experimental Procedure

The raw materials employed in this study consisted of precipitated calcium carbonate, alumina and ferric oxide.

Analyses of these materials are given in Table I.

TABLE I

ANALYSIS OF PURIFIED RAW MATERIALS[8]

	Calcium carbonate	Alumina	Ferric oxide
SiO_2	nil	0.01	
Al_2O_3	0.08	98.50	...
Fe_2O_3	.01	0.002	99.15
FeO	...	...	nil
CaO	55.73	...	...
MgO	0.01	...	...
Alkalies	.04		
CO_2	44.10	...	...
SO_3	trace	trace	nil
Cl	trace	trace	...
Loss on ignition	...	1.43	0.93

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[8] By H. C. Stecker.

The general principles involved in phase equilibria studies and the methods of experimentation have been very fully discussed by Rankin and Wright.[5]

The samples for study were prepared by mixing the finely powdered raw materials in a beaker with distilled water. These mixtures were placed on a hot-plate and stirred several times as evaporation proceeded to prevent segregation. When dry the mixtures were melted in platinum in an electric resistance furnace.[9] These melts of about 20 g. each were crushed in a steel mortar and ground in an agate mortar for use in the experiments described later.

Sosman and Hostetter[10] have shown that the dissociation of ferric oxide to ferro-ferric oxide increases with rise in temperature and time of heating. To minimize this dissociation as far as possible these preliminary samples were melted in an interval of about twenty minutes and at as low a temperature as possible. After a few samples had been studied the temperatures at which the others would melt could be estimated.

Crystallization was found to be very rapid in melts in this system, as it is in the $CaO-Fe_2O_3$[6] and $CaO-Fe_2O_3-SiO_2$[11] systems. Many of the melts obtained as described above crystallized completely so that their crystalline phases could be studied without additional treatment. Small charges of those that were not entirely crystallized were remelted in the quenching furnace[11] and cooled slowly to allow complete crystallization.

The crystalline phases were studied microscopically and their indices of refraction determined by the immersion method. The necessary high index media were prepared by the methods described by Larsen and Merwin[12] and by Brownmiller.[13]

Undercooled glasses could not be obtained by quenching melts in this system. It was necessary, therefore, to determine the melting relations by means of heating curves and to deduce the phase relations from the microscopic and heating curve data with the aid of the phase rule. This method is not so accurate nor so satisfactory as the quenching method, but it is believed that the phase relations reported herein are correct. Further work will be necessary to establish some of the boundary curves more exactly and to clear up other minor points in this part of the system.

Experimental Results

One ternary compound was found in the system $CaO-Al_2O_3-Fe_2O_3$. It has the oxide formula $4CaO.Al_2O_3.Fe_2O_3$ and the composition[14] CaO,

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[9] Hansen and Bogue, *Ind. Eng. Chem.*, *19*, 1260 (1927).

[10] Sosman and Hostetter, THIS JOURNAL, 38, 1188 (1916).

[11] Hansen and Bogue, *ibid.*, 48, 1261 (1926).

[12] Larsen and Merwin, Am. J. *Sci.*, 34, 42 (1912).

[13] Brownmiller, *Am. Mineralogist*, 12, *43* (1927).

[14] All compositions are given in percentage by weight.

46.1%; Al_2O_3, 21.0%; Fe_2O_3, 32.9%. It melts[15] congruently at 1415 ± 5°. This compound forms easily from the finely powdered components at temperatures well below its melting point. Its density[16] was found to be 3.77.

The optical properties of $4CaO.Al_2O_3.Fe_2O_3$ are as follows: biaxial, negative, with a medium optic axial angle. $\alpha_{Li} = 1.96 \pm .01$, $\beta_{Li} = 2.01 \pm .01$, $\gamma_{Li} = 2.04 \pm .01$. The indices for the yellow mercury line ($\lambda = 578$) are $a = 1.98 \pm .01$, $\beta = 2.05 \pm .01$, $\gamma = 2.08 \pm .01$. Occasional polysynthetic twinning was observed. The compound often occurs as prismatic grains with extinction angle against the prismatic faces very small. Pleochroism γ = brown and a = yellow-brown.

$4CaO.Al_2O_3.Fe_2O_3$ and CaO form a eutectic mixture of the composition CaO, 56%; Al_2O_3, 17%; Fe_2O_3, 27%; which melts at 1395 ± 5°. A partial temperature-concentration diagram of this system is given in Fig. 2.

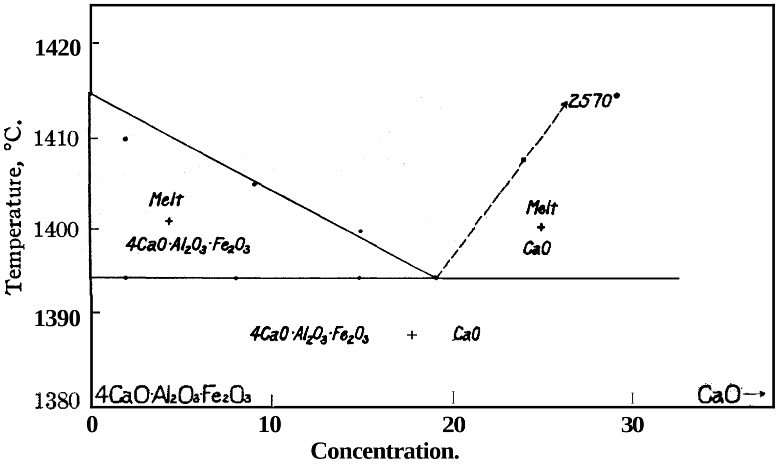

Fig. 2.—Partial temperature-concentration diagram of the system $4CaO.Al_2O_3.Fe_2O_3$-CaO.

$4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ form a complete series of solid solutions. The melting range of these solid solutions could not be determined from the heating curves. Only one distinct break was obtained on each of the heating curves. It appears, therefore, that the melting range of these solid solutions is very narrow, probably less than ten degrees. The temperatures of the observed thermal breaks are plotted against composition in Fig. 3. $2CaO.Fe_2O_3$ dissociates at 1435° into CaO and liquid. A thermal change was observed at this temperature in the heating curve obtained from the composition CaO, 41.5%; Al_2O_3, 1.5%; Fe_2O_3, 57.0% or $2CaO.Fe_2O_3$, 93% and $4CaO.Al_2O_3.Fe_2O_3$, 7%. This observation, in con-

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[15] All temperatures are given in centigrade degrees.

[16] Determined by Wm. Lerch using Le Chatelier's method, described in U. S. Bureau of Standards, Circular 33, 1917.

junction with the curve obtained in Fig. 3, indicates that CaO and solid solution are in equilibrium with liquid and vapor at 1435' in the above composition. That is, therefore, a quadruple invariant point. Charges of this composition were quenched from 1435' and examined microscopically for CaO. It was not possible, however, positively to identify CaO in those quenched charges.

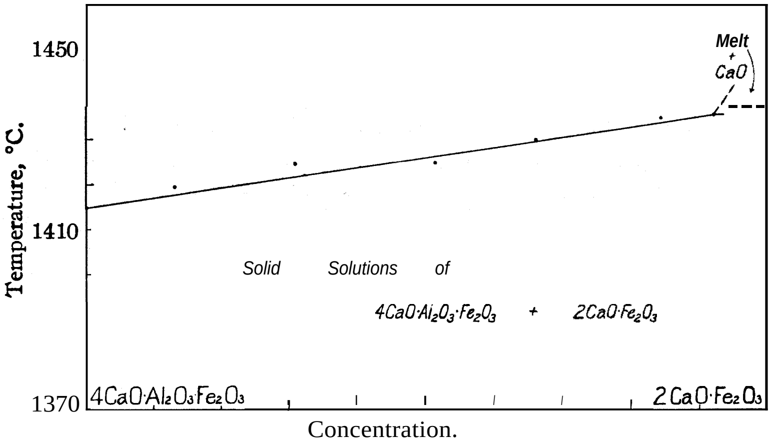

Fig. 3.—Temperature-concentration diagram showing the melting relations in the solid solution of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$.

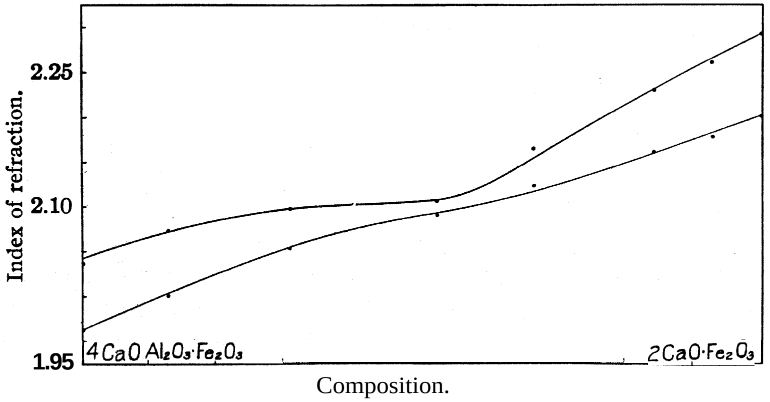

Fig. 4.—Indices of refraction of the solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ plotted against composition.

The α and γ indices of refraction of this series of solid solutions are shown graphically in Fig. 4. $2CaO.Fe_2O_3$ is biaxial, positive and $4CaO.Al_2O_3.$-Fe_2O_3 is biaxial, negative. The solid solutions rich in $2CaO.Fe_2O_3$ are positive while those rich in $4CaO.Al_2O_3.Fe_2O_3$ are negative. The exact composition at which the character changes has not been determined.

In Fig. 5 there are shown the fields below the line $CaO.Al_2O_3$-$CaO.Fe_2O_3$ which were studied in this investigation. The region above that line has not been explored. The five fields below this line show the regions in which the various compounds and solid solutions occur as the final products of crystallization of melts of these compositions.

In Fig. 6 the fields are shown in which CaO, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and solid solutions occur as primary phases. The dots in that figure represent the compositions studied during the investigation.

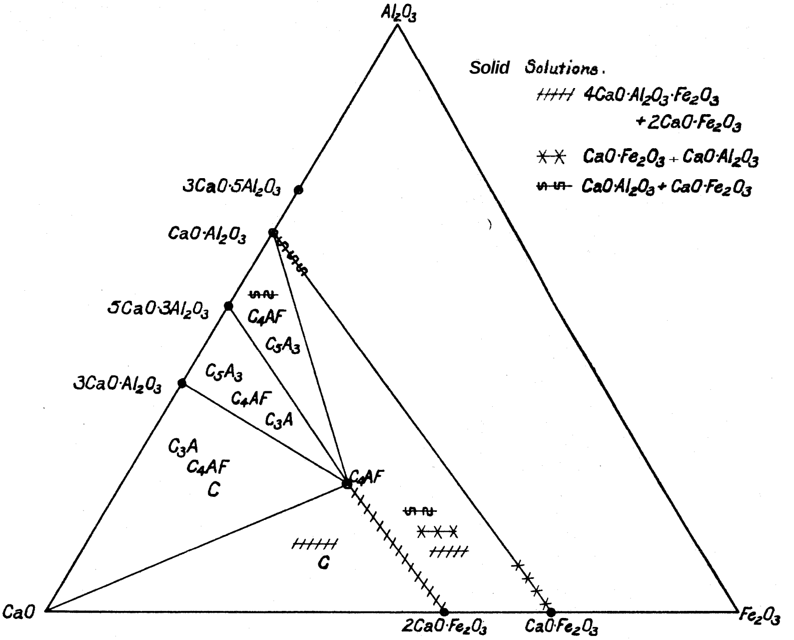

Fig. 5.—Diagram showing the final products of crystallization of melts in a portion of the ternary system CaO-Al_2O_3-Fe_2O_3.

The final melting temperatures of some of the compositions are given in that figure. These temperatures with those in the other figures are sufficient for the construction of a solid model of the liquidus surface of this portion of the system.

The two dashed lines (Pig. 6) radiating from the composition $4CaO.Al_2O_3.Fe_2O_3$ are not true boundary curves. A boundary curve is a line representing the compositions and temperatures at which two solid phases are in equilibrium with liquid and vapor. Since the compound $4CaO.Al_2O_3.Fe_2O_3$ forms a continuous series of solid solutions with $2CaO.Fe_2O_3$ there can be no boundary curve separating the fields in which $4CaO.Al_2O_3.Fe_2O_3$ and the solid solutions with $2CaO.Fe_2O_3$ separate as primary phases. It seems desirable, however, to indicate, in some manner, the compositions at which the primary phase changes from $4CaO.Al_2O_3.Fe_2O_3$ to a solid solution of $4CaO.Al_2O_3.Fe_2O_3$ with $2CaO.Fe_2O_3$.

The quintuple invariant point (Fig. 6) at which CaO, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, liquid and vapor are at equilibrium was found to have the composition CaO, 54%; Al_2O_3, 37%; Fe_2O_3, 9%; and to melt at 1345 ± 5°. If a line is drawn from $3CaO.Al_2O_3$ to $4CaO.Al_2O_3.Fe_2O_3$ in Fig. 6, as it is in Fig. 5, and the two figures are compared, it will be observed that CaO occurs as a primary phase in a part of the triangle $3CaO.Al_2O_3$—$4CaO.Al_2O_3.Fe_2O_3$—$5CaO.3Al_2O_3$. When crystallization is allowed to take place slowly in melts whose compositions fall within that triangle, the CaO combines with the liquid and disappears so that CaO is not a final product of crystallization in that field. It was found possible to quench the charges in which CaO occurs as the primary phase in this field and prevent its recombination. That made it possible to establish the quintuple point, referred to above, by both heating curves and quenches.

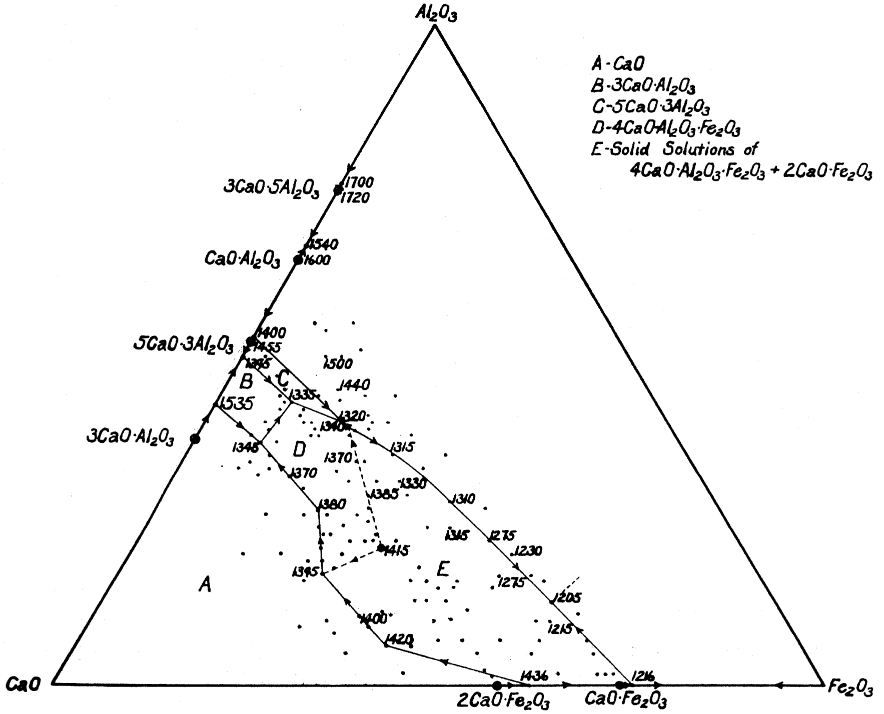

Fig. 6.—Diagram showing the fields in which CaO, $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$ and solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$ separate as primary phases. The dots represent the compositions studied.

$4CaO.Al_2O_3.Fe_2O_3$ and $5CaO.3Al_2O_3$ form a eutectic mixture of the composition CaO, 47%; Al_2O_3, 43%; Fe_2O_3, 10%; which melts at 1335 ± 5°. The temperature-concentration diagram of this system is given in Fig. 7.

The quintuple invariant point at which $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, liquid and vapor are at equilibrium appears to have very nearly the same composition and melting temperature as the binary eutectic of $5CaO.3Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$. Perhaps these two points can be differentiated when a greater number of samples are studied in the region of that point. This quintuple point, therefore, is given tentatively as CaO, 47%; Al_2O_3, 43%; Fe_2O_3, 10%; and 1355 ± 5°.

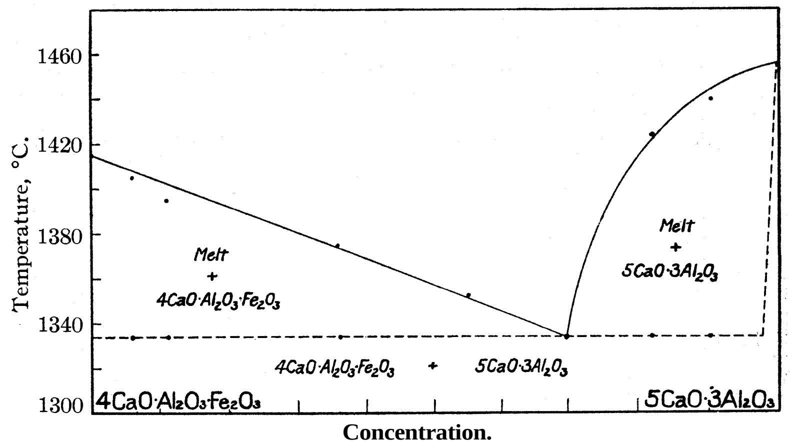

Fig. 7.—Temperature-concentration diagram of the system $4CaO.Al_2O_3.Fe_2O_3$-$5CaO.3Al_2O_3$.

$CaO.Al_2O_3$ takes up about 15% of $CaO.Fe_2O_3$ in solid solution and $CaO.Fe_2O_3$ appears to take up about 10% of $CaO.Al_2O_3$. The indices of refraction of $CaO.Al_2O_3$ increase from $\alpha_{Na} = 1.643$ and $\gamma_{Na} = 1.663$ to about 1.70 for α and 1.72 for γ. Those of $CaO.Fe_2O_3$ decrease from $\omega_{Li} = 2.465$ and ϵ_{Li} 2.345 to about 2.25 for ω and 2.13 for ϵ.

The melting relations existing between $CaO.Al_2O_3$ and $CaO.Fe_2O_3$ are shown in Fig. 8. It may be seen there that a eutectic mixture of the composition CaO, 28%; Al_2O_3, 13%; Fe_2O_3, 59% is formed. This mixture melts at 1205 ± 5°. This melting was observed in all of the samples within the four-sided figure (Fig. 5) $CaO.Al_2O_3$-$CaO.Fe_2O_3$-$2CaO.Fe_2O_3$.-$4CaO.Al_2O_3.Fe_2O_3$. In that region, when crystallization of the melts is completed, three crystalline phases are found. They are solid solutions of $CaO.Al_2O_3$ in $CaO.Fe_2O_3$, $CaO.Fe_2O_3$ in $CaO.Al_2O_3$ and $4CaO.Al_2O_3$.-Fe_2O_3 in $2CaO.Fe_2O_3$.

This point is, therefore, the quintuple invariant point at which the three solid solutions are in equilibrium with liquid and vapor. It would seem, therefore, that $CaO.Fe_2O_3$, which melts incongruently at 1216° into $2CaO.Fe_2O_3$ and liquid, in taking up $CaO.Al_2O_3$ in solid solution, has its incongruent melting point lowered to 1205 ± 5°. At this temperature this solid solution of $CaO.Al_2O_3$ in $CaO.Fe_2O_3$ dissociates into liquid and solid solutions of $2CaO.Fe_2O_3$ + $4CaO.Al_2O_3.Fe_2O_3$.

Samples having compositions falling on the line $CaO.Al_2O_3$-$4CaO.Al_2O_2.Fe_2O_3$ (Fig. 5) do not consist of those two compounds at equilibrium. The $CaO.Al_2O_3$ takes up some $CaO.Fe_2O_3$ which raises its indices of refraction. In some of the samples, small amounts of $5CaO.3Al_2O_3$ were found. The phase that should correspond to $4CaO.Al_2O_3.Fe_2O_3$ had somewhat lower indices of refraction. This phase was found to have α about 1.95 and γ 2.04 for the mercury yellow light.

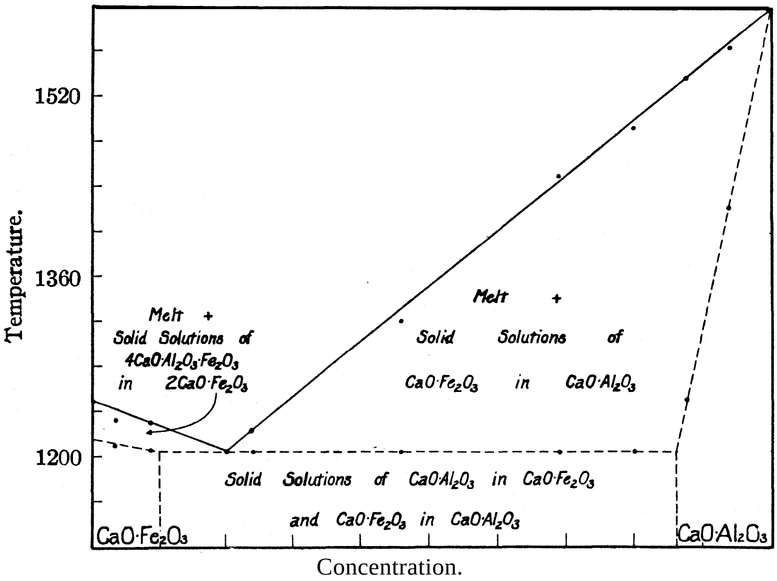

Fig. 8.—Diagram showing melting relations existing between $CaO.Fe_2O_3$ and $CaO.Al_2O_3$.

These results may be explained as follows. If $CaO.Al_2O_3$ takes up a certain amount of $CaO.Fe_2O_3$, the ratio of the remaining Al_2O_3 and CaO to the Fe_2O_3 is too great to form $4CaO.Al_2O_3.Fe_2O_3$ or its solid solutions with $2CaO.Fe_2O_3$. Therefore, some of the Al_2O_3 and CaO is combined as $5CaO.3Al_2O_3$. The other phase then is $4CaO.Al_2O_3.Fe_2O_3$ with a little $2CaO.Fe_2O_3$ in solution. From the lowered indices of refraction it would seem that $4CaO.Al_2O_3.Fe_2O_3$ and its solid solutions with $2CaO.Fe_2O_3$ are capable of taking up very small amounts of $CaO.Al_2O_3$ in solid solution. Therefore, in Fig. 5, the line $CaO.Al_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$ should be drawn from $CaO.Al_2O_2$ to some point on the solid solution line of 4CaO.-

$Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. The exact course of this line has not been established and is therefore shown as ending at $4CaO.Al_2O_3.Fe_2O_3$.

The indices of refraction of $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ are raised slightly in this system. Values as high as 1.735 were found for $3CaO.Al_2O_3$ and 1.720 for $5CaO.3Al_2O_3$.

None of the binary compounds of CaO with Al_2O_3 and Fe_2O_3 are found as the pure compounds within the ternary system as shown by their optical properties. The exact amount and nature of all of the solid solutions formed within this system have not been fully determined.

The compositions and melting temperatures of the quadruple and quintuple points found in this ternary system are given in Table II.

TABLE II

QUADRUPLE AND QUINTUPLE POINTS IN THE SYSTEM $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$

Crystalline phases	Composition, weight percentage CaO	Al_2O_3	Fe_2O_3	Temp., °C.
Quadruple Points				
CaO, $4CaO.Al_2O_3.Fe_2O_3$	56	17	26	1395 * 5
CaO, solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$	41.5	1.5	57.0	1435 ± 5
Quintuple Points				
CaO, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$	54	37	9	1345 ± 5
$3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, $5CaO.3Al_2O_3$	47	43	10	1335 ± 5
$4CaO.Al_2O_3.Fe_2O_3$, $5CaO.3Al_2O_3$, solid solutions of $CaO.Al_2O_3$ + $CaO.Fe_2O_3$	42	40	18	1320 ± 5
Solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ + $2CaO.Fe_2O_3$, $CaO.Al_2O_3$ + $CaO.Fe_2O_3$, $CaO.Fe_2O_3$ + $CaO.Al_2O_3$	28	13	59	1205 ± 5

In this paper the experimental results obtained in the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$ have been presented. The application of these findings to the problem of the constitution of portland cement will be presented in another paper.

The authors take pleasure in expressing their appreciation to Dr. Herbert Insley of the Bureau of Standards for advice and assistance in the microscopical studies.

Summary

A part of the $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$ system has been studied. One ternary compound of the composition $4CaO.Al_2O_3.Fe_2O_3$ was found in this part of the system. Its melting point and optical properties have been determined.

$2CaO.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ form a complete series of solid solutions. The melting relations and optical properties of these solutions are given.

$CaO.Al_2O_3$ and $CaO.Fe_2O_3$ form limited solid solutions with each other.

$3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$ have higher indices of refraction than they have in the binary system.

The fields in which CaO, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and solid solutions of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ separate as primary phases from these ternary melts are shown diagrammatically.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 21]

A RESISTANCE WIRE TO BE USED IN THE CHEMICAL LABORATORY

BY JEAN PICCARD

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Resistance coils which must have a perfectly constant resistance are always made of constantan (identical with ideal) or of manganin, as the resistances of both alloys are nearly independent of the temperature. These wires corrode easily. Nevertheless, the bad surface quality due to this corrosion causes no inconvenience since the whole coil is protected by paraffin. The very low thermoelectric force of manganin against copper renders its use almost imperative whenever direct current is involved. The somewhat better surface qualities of constantan are more than offset by its exceptionally high thermoelectric force against copper.

If, however, a measuring wire with slide contact is needed, as in the Wheatstone Bridge, then one faces an entirely different problem. One does not need in this case the very low temperature coefficient of the resistance because the different parts of the wire have nearly the same temperature, but one needs a wire with a bright surface which is not attacked either by the air or by the acid fumes of the laboratory. For this reason many authors favor the use of platinum wire. Its surface remains always perfectly clean, but its electric resistance has too high a temperature coefficient. It increases by 30 to 40% if the temperature rises from 0 to 100°, so that even the small changes of temperature which one produces when moving the contact slide with the hand have a noticeable effect on the position of the zero point.

The best resistance wire for Wheatstone Bridges, which, on request, was offered by Hereus for the use in the chemical laboratory, is platin-iridium. Apart from its very high price, however, it still has too high a temperature coefficient. An American company which manufactures resistance wires as a specialty was also unable to make us any satisfactory offer.

The question arose as to whether one could not replace the copper in constantan (60% Cu + 40% Ni) by the more noble metals of the same group, silver or gold. Since the jewelers recently began to use nickel-gold alloys called white gold, our first experiments were made with four of these alloys found on the market. One of them, a 14 K. white gold, was found to replace most favorably the constantan or the platinum measuring wire of the Wheatstone Bridge. Its electrical, chemical and mechanical properties make it a nearly ideal alloy for our purpose, especially if one is working with alternating current, as one generally is in the chemical laboratory. Its thermoelectric force against copper, although only half as large as that of constantan, is still too large to allow the substitution of manganin by the new alloy if very accurate measurements have to be made with direct current.

Prom a mechanical point of view, too, the new gold alloy has remarkably fine qualities. It is easy to pull thin wires of it; the alloy is hard enough to eliminate all abrasion at the contact point and it has an exceptionally high tensile strength, about 125 kg./sq. mm. This is four times more than constantan, even more than ordinary steel wire. One has, of course, a great advantage in being able to pull a measuring wire quite tightly without fear of breaking it.

The following table contains some of our results.

TABLE I

EFFECT OF CHEMICALS

	Ammonia	Concd. HCl	Concd. HNO_3
Constantan	Corrodes quickly	Dissolves slowly	Dissolves rapidly
14 K. white gold	No action	No action	Extracts Ni and Cu
18 K. white gold	No action	No action	No action

ELECTRIC QUALITIES

	Resistance, $10^4 \rho$	Temp. coefficient, $10^{-4} \cdot \frac{1}{\rho} \cdot \frac{d\rho}{dt}$	Thermoelectric force against copper, M. V./100°
Platinum, c. p.	0.126	38.0	−0.75
Constantan	.49	0.2	+4.5
14 K. white gold	.42	2.2	+2.6
18 K. white gold	.38	4.2	+3.82

The question further arose whether or not this temperature coefficient of 2.2 of the 14 K. white gold would still be too high to allow the use of the alloy for our purpose. This question was solved in the following way. A Wheatstone Bridge was constructed with a 100cm. long measuring wire of ordinary platinum, the temperature coefficient of which was 25, that is, more than 10 times that of the 14 K. white gold. When the zero point was about in the middle of the measuring wire, one side of the wire was touched with the hand and the displacement of the zero point observed. Then a radiator was turned on, on one side of the bridge or, the outside temperature being at freezing, a window was opened so that the draft came sideways onto the measuring wire. The zero point was of course displaced but even under these extreme conditions the displacement was never more than 1 mm. Hence with the 14 K. white gold wire used under these conditions the faults would always have been less than 0.1 mm. That means that under ordinary conditions or even under bad conditions the temperature coefficient of the 14 K. white gold measuring wire will never be the cause of any noticeable error.

Summary

White gold,[1] which has already partially replaced platinum in jewelry, replaces it advantageously in the alternating current Wheatstone Bridge when the latter is used in a chemical laboratory where constantan corrodes too rapidly. Constantan, exposed to the air of the laboratory, had to be cleaned after a few weeks, while white gold still gave perfectly good contacts after ten months.

Good surface qualities of the measuring wire are of the greatest importance, especially in modern laboratory technique where amplifiers are used in connection with very weak currents.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY, HARVARD UNIVERSITY]

A REVISION OF THE ATOMIC WEIGHT OF TITANIUM. III
THE ANALYSIS OF TITANIUM TETRABROMIDE

BY GREGORY PAUL BAXTER AND ALBERT QUIGG BUTLER

RECEIVED DECEMBER 19, 1927 PUBLISHED FEBRUARY 4, 1928

In two recent papers[1] the purification and analysis of titanium tetrachloride are described. The atomic weight of titanium computed from the experimental results is 47.90, a value considerably lower than that obtained by Thorpe, 48.1, which has been in use for some time. As a check on our recent work we have prepared and analyzed pure titanium tetrabromide and have obtained the same value as that found by analysis of the tetrachloride. Although in outline the two methods are similar, yet the differences in the physical and chemical properties of the compounds involved make it improbable that both results are affected by constant errors to the same extent.

Purification of Materials

Water, nitric acid, silver and bromine were purified by the methods usual when extreme refinement is necessary.[2]

Carbon was prepared from rock candy crystals, by charring, followed

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[1] 14 K. white gold wire similar to the one described above can now be obtained from Baker & Co., Inc., Newark, N. J.

[1] (a) Baxter and Fertig, THIS JOURNAL, 45, 1228 (1923); (b) Baxter and Butler, *ibid.*, 48, 3117 (1926).

[2] See, for instance, Baxter and Grover, *ibid.*, 37, 1028 (1915).

by ignition first in a covered porcelain crucible, then in an exhausted quartz tube.

Arsenic trioxide was several times recrystallized, once from very dilute hydrochloric acid, then from water. The product was chloride free.

Helium was very kindly provided by the U. S. Navy Department. It was purified and dried by being passed over concentrated sulfuric acid, hot calcium, hot copper oxide, hot copper, silver nitrate solution, solid potassium hydroxide, concentrated sulfuric acid and phosphorus pentoxide, in an all-glass apparatus. This gas may have contained a trace of hydrogen formed by decomposition of traces of water by the copper, but since this impurity could only result in the production of a small amount of hydrogen bromide in the synthesis of the titanium tetrabromide, it was allowed to remain.

Titanium tetrabromide was prepared by the action of bromine at a high temperature on (a) metallic titanium, or (b) a mixture of carbon and titanium dioxide. Because of the action of nitrogen on titanium at high temperatures, helium was used as the carrier of the bromine. The products of several experiments were combined for the final purification by fractional distillation.

Titanium dioxide kindly furnished by the Valentine Valspar Co. served as the starting point in every case. To prepare metallic titanium the powdered dioxide was mixed with a 50% excess of magnesium powder by grinding and the reaction was started by igniting the mixture in a muffle. The product was extracted with an excess of hydrobromic acid and the residue digested with two successive portions of fresh acid at nearly boiling temperature Washing by decantation followed, with centrifugal settling of the rather finely divided titanium in order to promote efficiency. The clean metal was dried on an electric hot-plate and after powdering was ignited in a high vacuum.

In the preparation of the tetrabromide from titanium, the metal was contained in a hard glass tube connected at one end by a ground joint with the apparatus for purifying helium and charging it with bromine, at the other by means of a ground joint of large diameter with a glass bulb which served as condenser. The reaction tube sloped toward the receiver at all points. Because of the high boiling point of the tetrabromide, 238°, especial cooling of the condenser was unnecessary. The helium could be passed either directly into the reaction tube or through bromine in a bubbling flask and then over the titanium. In a run the apparatus was first swept out with helium. Then the current of helium was directed through the bromine, and the titanium was heated electrically to redness. At the same time the bromine was warmed to increase its vapor pressure. The product, judging from the color, was at first nearly free from bromine, but before long uncombined bromine began to accompany the tetrabromide to a marked extent. Two experiments of this sort were both interrupted by accidents to the apparatus so that the total resulting quantity of tetrabromide was not more than 60–70 g.

In a third experiment, instead of titanium, a mixture of ground, ignited titanium dioxide with a considerable excess of carbon was employed. The result of this experiment was satisfactory so far as yield is concerned although the former method gave every indication of being equally good under favorable conditions. About 200 g. was obtained from this experiment.

The material produced by the two methods was next separately freed from a large part of the excess of bromine by exhausting the containers with an efficient water pump while at the same time the container was warmed in a paraffin bath and the liquid boiled vigorously to flush out as much of the residual air as possible. The containers were then closed by fusing a capillary connection. Both containers were then connected through special fused-in joints (a, Fig. 1)[3] to a large bulb which was also connected with a Hempel fractionating column terminating in a special joint. By means of a Gaede mercury pump this bulb together with the fractionating column was thoroughly exhausted and sealed off. In succession the special joint of each container was opened and the contents distilled into the receiving bulb. Then the container was sealed off by fusing a capillary. The combined sample, of about 100 ml. in volume, was a reddish-brown mass, partly liquid owing to the excess of bromine.

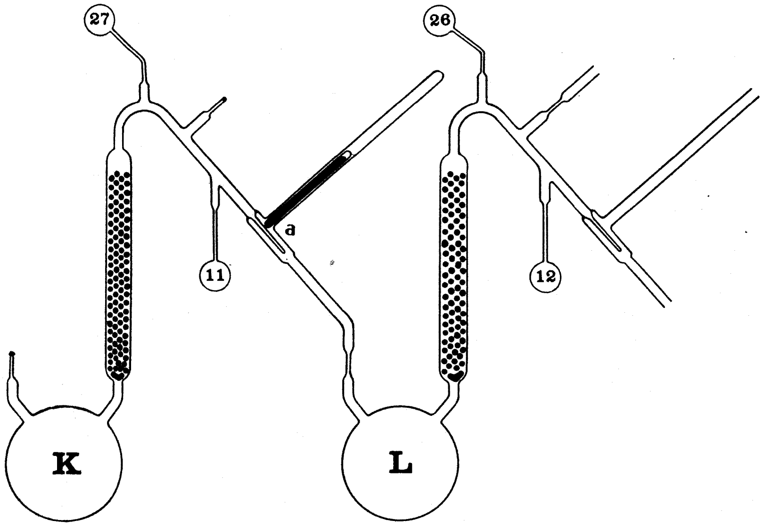

Fig. 1.

Fractional distillation in exhausted apparatus followed. The apparatus was modified slightly from one distillation to another but in general a distillation was carried out as follows. The material was contained in the exhausted bulb K (Fig. 1) attached through the Hempel column and the special joint to the receiving bulb L, which in turn was attached to a similar system also thoroughly exhausted. The special joint was then opened by means of the hammer weighted with mercury. The still K was warmed to about 150" in a paraffin-bath and the most volatile fraction of the tetrabromide was collected in the bulb 11 which was disconnected by sealing the capillary. The greater part of the tetrabromide was distilled into L, and the capillary was sealed. The residue in K was then collected in 27 and sealed off. After the receiver L had been connected to a similar exhausted system, the distillation process was repeated. During the distillation the fractionating column was jacketed with asbestos paper. Although

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[3] (a) Bruner and Bekier, *Z. Electrochem.*, 18, 369 (1912); (b) Briscoe and Little, *J.* ***Chem. Soc.***, *105,* 1324 *(1914);* (c) Baxter and Starkweather, THIS JOURNAL, 42, 907 (1920).

refluxing was very efficient, choking of the column was negligible. In all, 18 such fractional distillations were carried out. After the third, sixth and ninth distillation cracks in the apparatus necessitated transference by pouring to another bulb, which was exhausted while hot by means of a water pump and sealed off. The last nine distillations were, however, free from any such accident.

The complete course of the fractional distillation is shown in Fig. 2. The large lettered circles represent separate distillations, the small circles the fractions removed. The fractions to the right are the more volatile ones, while the fractions to the left are the less volatile ones. The fractions analyzed, as well as the atomic weights found in the analyses, are given in the figure.

Probable impurities in the crude tetrabromide included, besides bromine, hydrogen bromide from hydrolysis of the titanium tetrabromide when exposed to moisture in the air, carbon tetrabromide from action of bromine on charcoal and silicon tetrabromide from silicon contained in the titanium dioxide or from the glass. The boiling points and the effect on the atomic weight of titanium of one-tenth of one per cent. impurity of each are given in Table I.

The removal of the bromine was very rapid, for no evidence of its presence was obtained after the first three distillations. Presumably the still more volatile hydrogen bromide was removed at the same time. No tests for the other impurities were made, since all past experience with the distillation of inorganic halides has indicated that, when boiling points are as widely separated as in this case, separation is very rapid. Furthermore, the constancy in

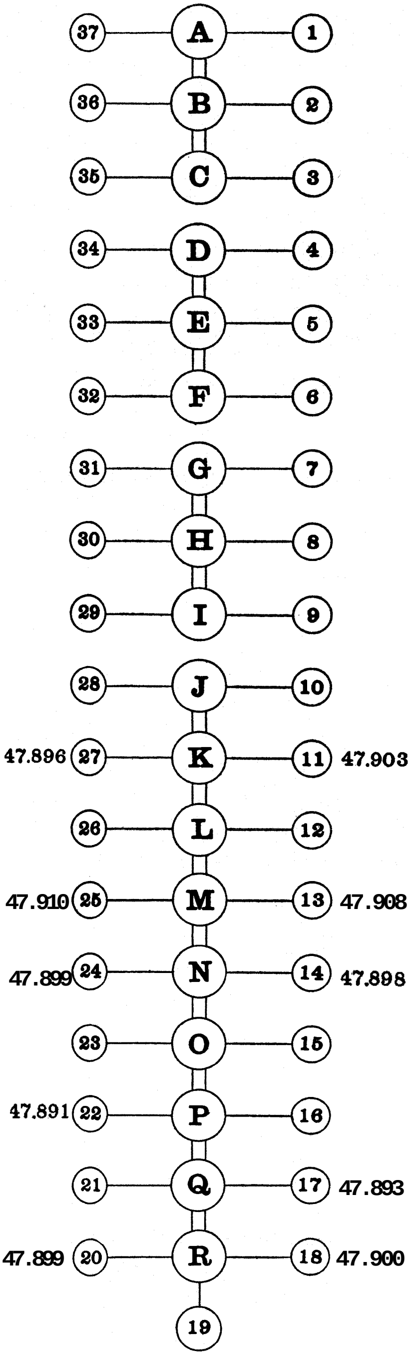

Fig. 2.

TABLE I

	B. p., °C.	Effect of 0.1% of impurity
$TiBr_4$	230	....
HBr	−69	−0.050
Br_2	59	− .055
CBr_4	190	− .040
$SiBr_4$	153	− .021

composition of the fractions of the tetrabromide after the initial stages in the fractional distillation is evidence in the same direction. At any rate it is clear that purification by this method had reached a limit.

The final product was a lemon-yellow solid at ordinary temperatures and melted to a somewhat darker liquid.

Method of Analysis

The titanium tetrabromide was analyzed as in the case of the tetrachloride by solution in dilute nitric acid and comparison of the solution with silver. Since nitric acid slowly acts on the tetrabromide to liberate bromine, a small amount of arsenious acid was added to the nitric acid beforehand. Under these conditions no odor or color of bromine was ever detected.

A still more rigorous test for possible loss of bromine was made by dissolving one fraction of the tetrabromide in nitric acid containing arsenious acid, and drawing air slowly for two hours over or through the solution and then through a solution of ammonia. The latter was finally evaporated to small volume and tested for bromide by comparison with known quantities in a nephelometer. Various concentrations of bromide and nitric acid were used.

TABLE II

Concn. of $TiBr_4$, %	Concn. of HNO_3, normality	Bromide found, mg.	Concn. of $TiBr_4$, %	Concn. of HNO_3, normality	Bromide found, mg.
1.0	0.5	0.15	1.0	0.25	0.10
0.5	.5	.005	0.5	.20	.04
.5	.5	.3	.75	.18	.10
.5	.4	.05	.5	.12	.01
.5	.4	.15	.5	.12	.005
.5	.3	.10	.5	.12	.02
.5	.25	.005	.5	.12	.000
.5	.25	.005	.5	.10	.05

Since the loss of bromide from the solution seemed to be negligible at concentrations of nitric acid around 0.1 N, this concentration of nitric acid was used for the solution of the titanium tetrabromide.

The more important details of the method of analysis were as follows. In order to find the density of the glass bulb containing the tetrabromide, it was weighed first submerged in water of known temperature, and then, after being cleaned and dried, by substitution in air of known density.[4]

The weighed bulb was next broken under one liter of 0.1 N nitric acid containing 0.1 g. of dissolved arsenious oxide in a heavy-walled, glass-stoppered flask, and the solution was allowed to stand for several hours. No turbidity ever appeared and the hydrobromic acid fumes formed at first were quickly absorbed by the solution. The solution was then filtered into the glass-stoppered precipitating flask or bottle, through a weighed platinum-sponge Gooch crucible, on which the fragments of the glass bulb were collected after they had been washed with pure water. In order to prevent the retention of titanic acid, the crucible and the glass were further washed with hot 6 N nitric acid, and after being washed with water and dried at 250° were weighed. A second treatment with nitric acid ordinarily did not produce a change in weight of more than 0.02 mg., but in four experiments a third treatment was necessary before constant weight was secured. This method of collecting and weighing the glass was found satisfactory in the analysis of titanium tetrachloride.

The weight of titanium tetrabromide was obtained as the difference between the weight of the bulb and the weight of the glass, both corrected to vacuum. Very nearly the exact weight of pure silver necessary to combine with the tetrabromide was dissolved in nitric acid with especial precautions to avoid loss by spattering and, after dilution until approximately 0.1 N, the solution was slowly added to the bromide solution, which at this stage also was as dilute as 0.1 N and in many cases no more than 0.05 N. Thorough shaking and standing for several days followed. With the aid of a nephelometer the bromide and silver in the solution were adjusted to equivalence by the addition of hundredth normal solutions. Several weeks always elapsed between the precipitation and the final adjustment of the end-point, so that occluded material had abundant opportunity for being extracted from the precipitate of silver bromide.

No attempt was made to estimate the silver bromide quantitatively, since in the analysis of the tetrachloride the silver chloride was found to be badly contaminated with titanium compounds.

Weights were standardized by the substitution method of Richards.[5] Vacuum corrections were applied as follows.

	Density	Vacuum correction per gram
Weights	8.3	
Silver	10.49	−0.000031
Glass	2.5	+ .000335
Air	0.001293 (0° and 760 mm.)	

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[4] Baxter, THIS JOURNAL, 43, 1317 (1921).

[5] Richards, *ibid.*, 22, 144 (1900).

Results

TABLE III

ATOMIC WEIGHT OF TITANIUM

$TiBr_4:4Ag$ Ag = 107.88   Br = 79.916

Analysis	Sample of $TiBr_4$	Weight of $TiBr_4$ in vacuum, g.	Weight of Ag in vacuum, g.	Weight of Ag added or subtracted in soln., g.	Corrected weight of Ag in vacuum, g.	$TiBr_4:4Ag$ Ratio,	Atomic weight of titanium
1	11	10.02147	11.76552	−0.00040	11.76512	0.851796	47.903
2	13	9.20373	10.80523	− .00030	10.80493	.851808	47.908
3	25	4.33488	5.08816	+ .00085	5.08901	.851812	47.910
4	27	8.22722	9.65971	− .00085	9.65886	.851780	47.896
5	14	9.59208	11.26112	+ .00004	11.26116	.851784	47.898
6	24	5.09864	5.98572	+ .00010	5.98582	.851786	47.899
7	17	5.29301	6.21401	+ .00010	6.21411	.851773	47.893
8	22	6.53582	7.67314	+ .00010	7.67324	.851768	47.891
9	18	6.14520	7.21432	+ .00015	7.21447	.851788	47.900
10	20	4.72253	5.54423	+ .00004	5.54427	.851786	47.899
					Average	.851788	47.900

Discussion

The extreme deviation of the calculated values for the atomic weight of titanium is 0.019 unit, but six of the results fall within a range of 0.007 unit. The "probable error" of the mean is 0.0013 unit, but it is far from certain that the accuracy of the final average is as great as this, owing to constant errors which it is impossible entirely to eliminate.

If the results are arranged in the order of decreasing volatility of the fractions of tetrabromide no trend is apparent, for the average of the first five results is 47.900, and the average of the last five 47.899.

Fraction of $TiBr_4$	Atomic weight of titanium	Fraction of $TiBr_4$	Atomic weight of titanium
11	47.903	20	47.899
13	47.908	22	47.891
14	47.898	24	47.899
17	47.893	25	47.910
18	47.900	27	47.896

In his initial examination of titanium in the mass spectrograph, Aston[6] found doubtful indications of an isotope of mass 50 besides the main isotope of mass 48, but apparently this indication has not been confirmed. The atomic weight 47.90 is in accord with the general rule that the masses of individual isotopes fall short of integral values when the mass number is between 20 and 200, but leads to a "packing fraction" nearly three times as large as that corresponding to Aston's curve connecting packing fraction with mass number.[7] This discrepancy may be due to an undiscovered isotope of mass number less than 48.

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[6] Aston, *Phil. Mag.*, **47,** 397 (1924).

[7] Aston, *Proc. Roy. Soc. (London)*, **115A,** 510 (1927).

Under the conditions of the distillation no separation of the bromine isotopes is to be feared, as the constancy in composition of the fractionated material also indicates.

The analyses of titanium tetrachloride and titanium tetrabromide thus agree in yielding the value 47.90 for the atomic weight of titanium.

This research has been assisted by a grant from the Bache Fund of the National Academy of Sciences.

CAMBRIDGE, MASSACHUSETTS

NOTES

Alkali Earth Metals in Saccharate Solutions and their Use in Alkalimetry.—Theoretically it would be most desirable to find some substance the equivalent weight of which could be directly weighed out, put into solution and diluted to a given volume to yield a standard of predetermined normality that would not require standardization or adjustment. The writer has been carrying on some work in an attempt to realize, partially at least, this ideal.

To this end different materials that would yield calcium oxide have been converted to that substance or to calcium hydroxide and have been dissolved to form a standard solution in a 30% cane sugar. These attempts were successful in so far as the attainment of the final results were concerned, but so much time was consumed that the method was not considered practical. In the course of further investigations, it was found that samples of metallic calcium in the form of 0.05 inch wire and about 96% pure went into solution at the rate of 1 g. in about eight minutes, on the average. In the ten cases tried a solution of predetermined normality was obtained, employing, of course, a correction factor to allow for the impurities. The calcium was obtained from the General Electric Company and, though impure, was so uniform that samples from different parts of the lots were found to yield identical solutions. The chief impurity is metallic magnesium which, together with its oxide, is almost insoluble in 30% sucrose, a fact that might be employed in separating small amounts of magnesium from large percentages of calcium especially in the analysis of metallic calcium. It would seem easy to eliminate this impurity by employing pure calcium chloride as an electrolyte instead of that obtained as a by-product from magnesian bitterns.

Another source of impurity is the rapid tarnishing of clean surfaces of metallic calcium when exposed to moist air, as reported in the literature. The film so formed is slow to appear in ordinary air and since it is very thin and consists of a high calcium compound, the error from this source seems negligible; however, it can easily be sandpapered off from the warm metal much as rust is removed from standard iron wire. The warm calcium which does not tarnish readily can then be enclosed in a suitable weighing bottle, cooled and weighed. The metal used in the above experiments was weighed in the open air with excellent results.

Some doubts seem to exist as to whether it would be feasible to produce C. P. metallic calcium. The very recent notable success of Syracuse University in producing 99.9+% metallic barium, a more reactive metal than calcium, should satisfactorily answer this question. In addition, The American Magnesium Corporation in a letter to the writer stated that that company has produced metallic calcium analyzing 99.98% metal. Moreover, it is common knowledge that very pure metallic sodium, still more reactive than the alkali-earth metals, has been produced commercially for years in enormous quantities at a reasonable price.

The size of wire is an important factor in the production of metal suitable for analytical work. Half-inch sticks are too large, as solubility is too slow; 0.05 inch wire is rather small, as the length of a tenth-equivalent is too great for convenience. One-eighth inch sticks would probably be most suitable so that the length of a tenth-equivalent weight would be convenient.

To ascertain whether or not the solution of calcium saccharate so prepared was suitable for general analytical work, titrations of carbonic acid, acid potassium phthalate and succinic acid were carried out with satisfactory results, employing the common indicators. To further test out the solution in actual practice, samples were distributed to m'embers of the chemical faculty for general use. These reported that the solutions were as satisfactory as the bases commonly employed.

The purpose of these notes is to interest, if possible, some producer of metallic calcium to furnish this element in sufficient purity to satisfy the requirements as outlined and at a non-prohibitive price. The successful accomplishment of this object seems attainable by attention to the exclusion of magnesium from the electrolyte employed in the method now used. The financial rewards of such a course seem to be assured because it would enable the chemist to prepare, with a single weighing, a standard alkali of predetermined normality, carbonate free and ready for use without previous standardization by an auxiliary substance.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
UNIVERSITY OF OKLAHOMA
NORMAN, OKLAHOMA

A. C. SHEAD

RECEIVED OCTOBER 10, 1927
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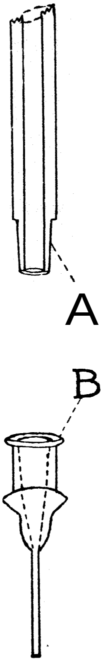
A Pipet for **Micro-Analyses.**—The accurate delivery of small amounts of fluid is essential for micro-analyses. Folin[1] has stated that the Ostwald pipet is accurate to the order of 0.1%. Van Slyke and Neill[2] have improved this. They calibrate between marks and place a stopcock under the bottom mark. Their pipet is excellent for introducing fluids into the Van Slyke gas apparatus but is not equally practicable for other uses. Unless the end is washed a variable and unknown amount of fluid clings to the tip.

The pipet which we use is a modification of Van Slyke's, with a glass Luer adapter sealed to the bottom end. This ground end fits snugly into a hypodermic needle B of small gage, 18–23, which is cut off horizontally and ground on a stone. Trevan and Bainbridge[3] have shown that drops of the order of 0.00015 cc. can be removed from such a needle tip. For corrosive liquids a platinum needle may be used.

A test of the amount delivered indicated a surprising degree of accuracy. One worker obtained for a given pipet the following weights of water: 0.9982, 0.9981 and 0.9980 g. A second investigator weighed the water delivered from the same pipet as 0.9982 and 0.9983 g.



A, ground glass Luer adapter which fits into B; B, a hypodermic needle Drawing is actual size.

Fig. 1

Contribution from the
Laboratory of
Physiological Chemistry
Yale University
New Haven, Connecticut

Alfred T. Shohl

Received November 12, 1927
Published February 4, 1928

Apparatus for **Micro-Filtration.**—The centrifuge tube technique for the separation and washing of precipitates has been very useful for micro-analyses. In the course of development of a method for potassium, however, a small amount of material was lost when the supernatant fluid was poured off. To overcome this difficulty the following form of apparatus was devised (Fig. 1).

The principle is that of a Caldwell crucible. The filter is made by mounting a one inch funnel in a Witt filtering apparatus (this is essentially a suction flask with a ground glass removable top so that the filtrate may be recovered in a small inner container. If the precipitate only is to be saved, an ordinary suction flask is satisfactory). Into the

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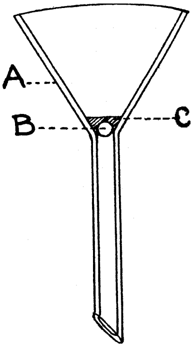
[1] Folin, J. *Biol. Chem.*, 21, 198 (1915).

[2] Van Slyke and Neill, *ibid.*, 61, 532 (1924).

[3] Trevan and Bainbridge, *Biochem.* J., 20, 423 (1926).

funnel, A, a glass pearl, B, is dropped and over the bead is poured a suspension of finely shredded asbestos, C, to form a layer about 1/32 of an inch thick. The mat is allowed to drain and suction is applied (see Fig. 1).



A—one inch glass funnel; B—small glass pearl or bead; C—mat of fine grained asbestos. Drawing is 3/4 actual size.

Fig 1

The precipitate and mother liquor are transferred to the micro-filter and the filtrate is removed by gentle suction. One drop of fluid is sufficient to wash the precipitate on the mat. With intermittent suction a precipitate can easily be washed five to ten times with one cc. of solution.

To remove the precipitate the funnel is inverted and a glass rod is inserted into the stem. Precipitates such as calcium, sodium, potassium, phosphorus, etc., that are to be dissolved before determination may be dissolved either on the mat, or in a separate container after removal together with the mat. In the latter case, a second filtration through the same apparatus gives a solution free of asbestos.

The materials for this micro-filter are at hand in every laboratory. They are inexpensive. During a year of use not a single determination has been lost.

CONTRIBUTION FROM THE LABORATORY
OF PHYSIOLOGICAL CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

ALFRED T. SHOHL

RECEIVED NOVEMBER 12, 1927
PUBLISHED FEBRUARY 4, 1928

CORRECTION

Through the work of Paul S. Roller[1] it has come to my attention that the signs of two terms in Equation 10 of my paper on titration[2] are incorrectly recorded. The term $3K_WK_A^{-2}$ in the coefficient of $(H^+)^3$ should be negative, as should also the last term of the equation. I wish also to confirm the result obtained by Roller by an independent method concerning the limiting strength of acid necessary for appearance of an inflection in titration with a strong base, the values of the ionization constants given in my paper for this case being too large, due to a numerical error, by one power of ten.

E. D. EASTMAN

RECEIVED NOVEMBER 15, 1927
PUBLISHED FEBRUARY 4, 1928

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[1] Roller, THIS JOURNAL, 50, 1 (1928).

[2] Eastman, *ibid.*, 47, 332 (1925).

Note on the Changes in Composition of Compressed Air after Long Storage in a Steel Cylinder.—In connection with a study of the composition of outdoor air,[1] a steel cylinder of compressed air was secured from the compressed air plant at the Laboratory of Technical Engineering of the Massachusetts Institute of Technology and brought to the Nutrition Laboratory of the Carnegie Institution in the fall of 1910 as a control on gas analyses made with outdoor air. Disregarding the earlier series of analyses in which the technique was developing, in the chemical composition of this gas the percentage of carbon dioxide was 0.032 and of oxygen was 20.870.[2]

The analyses were made with the exceedingly exact Sondén gas analysis apparatus, which is described in the cited monograph. The cylinder has remained in the Laboratory unused since that time. Recently the composition of the air has again been determined using the new form of the Carpenter gas analysis apparatus.[3] On the day on which these analyses were made, the composition of the outdoor air was reported as 0.030% for carbon dioxide and 20.940% for oxygen, the usual figures found with this apparatus Two analyses of the air in the cylinder gave identical figures, both for carbon dioxide and oxygen, as 0.024% for carbon dioxide and 20.321% for oxygen. In the compressing of gas in these cylinders naturally the larger amount of water is removed, and yet there is enough moisture in the cylinder to facilitate oxidation.

The decrease in oxygen percentage incidental to seventeen years' storage is explained by the oxidation. The decrease in carbon dioxide content can be explained only by the presence of alkaline material in the cylinder.

Summary.—Analyses of compressed air after seventeen years' storage in a steel cylinder gave evidence of a slight drop in carbon dioxide percentage and a drop of approximately 0.6% in oxygen percentage.

CONTRIBUTION FROM THE NUTRITION LABORATORY OF THE CARNEGIE INSTITUTION OF WASHINGTON
BOSTON, MASSACHUSETTS
ARTHUR F. SEREQUE

RECEIVED NOVEMBER 22, 1927
PUBLISHED FEBRUARY 4, 1928

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[1] See "Composition of the Atmosphere with Special Reference to Its Oxygen Content," by F. G. Benedict, Carnegie Institution of Washington, Publication No. 166, 1912.

[2] As no attempt was made to secure uncontaminated outdoor air in the air compressors, the fact that its composition differs from that of pure air is not of significance.

[3] "An Apparatus for the Exact Analysis of Air in Metabolism Investigations with Respiratory Exchange Chambers," by Thorne M. Carpenter, *Journal of Metabolic Research, 4,* 1 (1923).

[CONTRIBUTION FROM THE MAYO CLINIC AND THE MAYO FOUNDATION]

INSULIN AND AMINO ACID CATALYSIS

BY JOHN M. ORT

RECEIVED JUNE 20, 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

In a former paper[1] it was shown that in the presence of certain amino acids, the action of very dilute hydrogen peroxide on dextrose is hastened. Under the conditions of the experiments, other amino acids are without effect within six hours. This paper is a report of further studies on this action by the use of the oxidation-potential method. This time both dextrose and levulose were investigated. The effect of insulin on each was also determined, both in the presence and in the absence of the amino acids.

With the same technique as before, a study was made first on the influence of the rate of bubbles of the nitrogen gas which passed through the solutions, stirring them and freeing them from dissolved oxygen. In the former experiments the nitrogen passed through at a rate of approximately *25* bubbles a minute from the fire-polished end of a 6 mm. Pyrex capillary tube of 1 mm. bore, about 4 cm. below the surface of the liquid. In the experiments reported at this time, the rate of bubbles was approximately 2 a second. Doubling this rate did not have a significant effect on the shapes of the time-potential curves, in which form the data are presented.

The slower rate in the former experiments was considered safe since at that rate it was felt the nitrogen would completely carry out any oxygen that might diffuse into the chambers at the top, either through or around the rubber stoppers. On the other hand, substances reacting in the blood streams of animals are subjected to much more violent shaking and mixing than would be given by the twenty-five a minute rate. Therefore, it seems desirable to have present in the experiments the effect of the more rapid stirring, since it is hoped that the results may have some significance in connection with the mechanism of sugar oxidation in *vivo*.

In all experiments the solutions were first freed from most of the dissolved air by the very rapid passage of nitrogen (about 20 bubbles a second) for approximately one hour late in the afternoon. After this the rate was reduced to about 25 bubbles a minute in'the former experiments and to about 2 a second in this series, and the nitrogen allowed to bubble through the solutions at the slower rate overnight. The next morning the potentials were found to be changing but very slowly, and the dissolved air was assumed to be completely removed. Hydrogen peroxide was then added and the drifts of the oxidation potentials with time were followed. Longer periods of standing, before the addition of the hydrogen peroxide,

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[1] Ort and Bollman, THIS JOURNAL, 49,805–810 (1927).

did not change the results significantly. Neither did shorter periods, provided the removal of dissolved oxygen had proceeded far enough to develop within the solution a moderate reducing intensity of approximately −0.15 volt. When hydrogen peroxide was added much before this, the resultant oxidation potentials often rose to 0.3 volt and over. The latent reducing power of the sugars under these conditions seemed to be temporarily paralyzed, for recovery to the previous negative potentials was delayed. The same was true if too much hydrogen peroxide was added at one time.

It is again pointed out that the results of these experiments can have only a qualitative significance. In the absence of a single, definite, reversible, oxidation-reduction equilibrium no exactly reproducible potentials can be expected. It is only assumed that the differences in the general shapes of the curves correspond to actual differences in the courses of oxidation of dextrose and levulose by hydrogen peroxide under the various conditions studied.

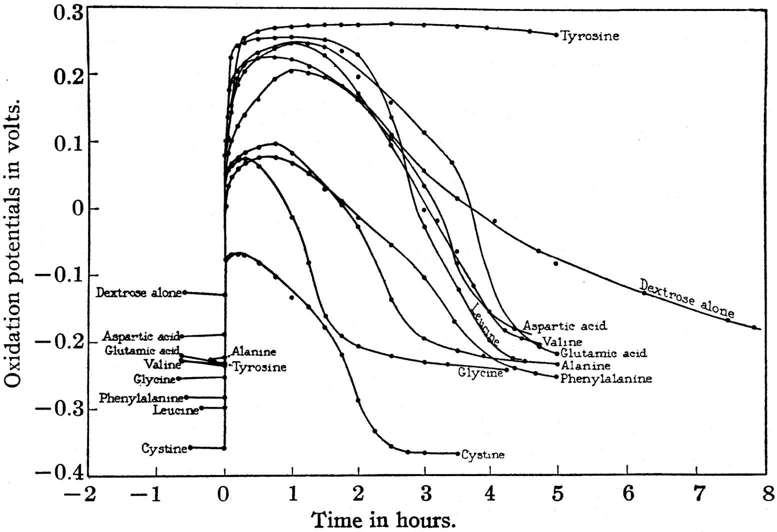

Fig. 1.—Dextrose and the amino acids.

Results of Experiments

Figure 1 shows the effect of several of the amino acids on the action of 0.5 cc. of 0.03% hydrogen peroxide added at time zero to a solution of 200 mg. of dextrose in a buffer at PH 10 and a temperature of 30°. The amount of amino acid present was 0.001 mole. With the exception of tyrosine, all had at least some accelerating action. This is somewhat different from the results published before. Glutamic acid and aspartic acid had little effect at the slower rate of bubbling, which is the only difference between the two sets of experiments. In Fig. 1, glycine, alanine and phenylalanine stand together as a group apart from valine, leucine, glutamic acid and aspartic acid. This grouping seems to parallel even closer the grouping, as shown by the latest work, according to specific dynamic action. Tyrosine alone, which has been found to have marked specific dynamic action, seems out of place. But with tyrosine in the experiments as performed in vitro, the solutions became more oxidizing than the others, under which conditions, as already mentioned, the reducing power of dextrose becomes temporarily paralyzed. In *vivo* the blood has a posing action, which would prevent such an oxidizing intensity. At least tyrosine seems to have an effect on the oxidation of dextrose somewhat different from that of the other amino acids studied.

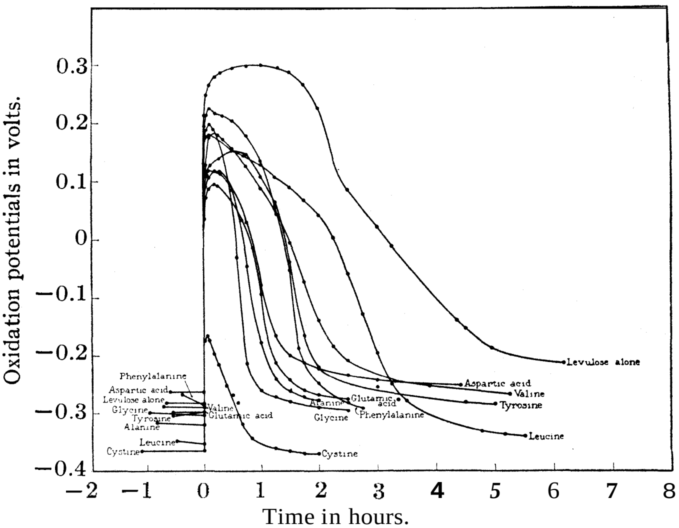

Fig. 2.—levulose and the amino acids.

Figure 2 shows the results of similar experiments on levulose. As would be expected, recovery occurs sooner and more rapidly than with dextrose. With the exception of cystine, which exists in solution in a reversible system, glycine, alanine, glutamic acid and aspartic acid are the most effective catalyzers. This division seems to have no relation whatever to specific dynamic action In comparing these curves to those in Fig. 1, it is interesting to note that for levulose as well as dextrose the rate of recovery is greatest in almost all cases in a region of oxidation potentials bordered very roughly by 0.05 and —0.15 volt. It can also be seen that in both cases the rate of fall in potentials drops off sharply in the neighborhood of —0.2 volt.

In Fig. 3 is shown the action of hydrogen peroxide on solutions of insulin and the amino acids, without any sugar. One cc. of Lilly's U 20 Illetin was added in each case at the start of the run, the other details being as before. With the exception of cystine no action was indicated. These

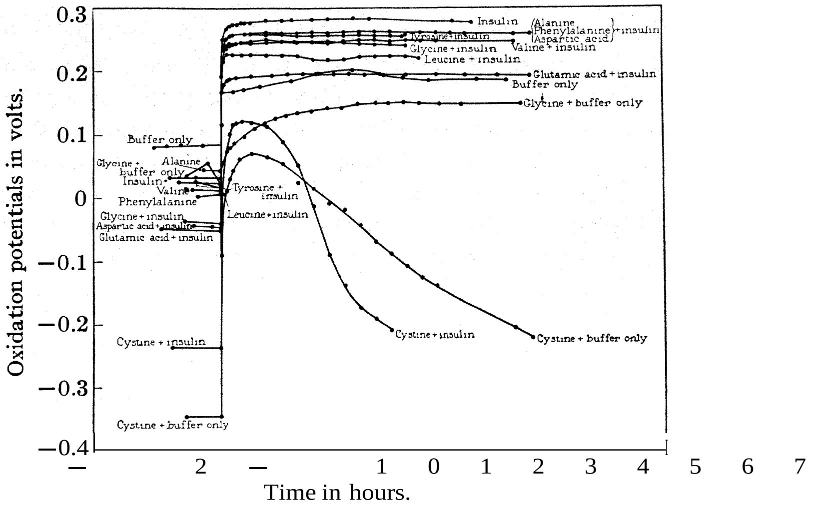

Fig. 3.—Insulin and the amino acids.

experiments were performed as controls for the studies with insulin on dextrose and levulose.

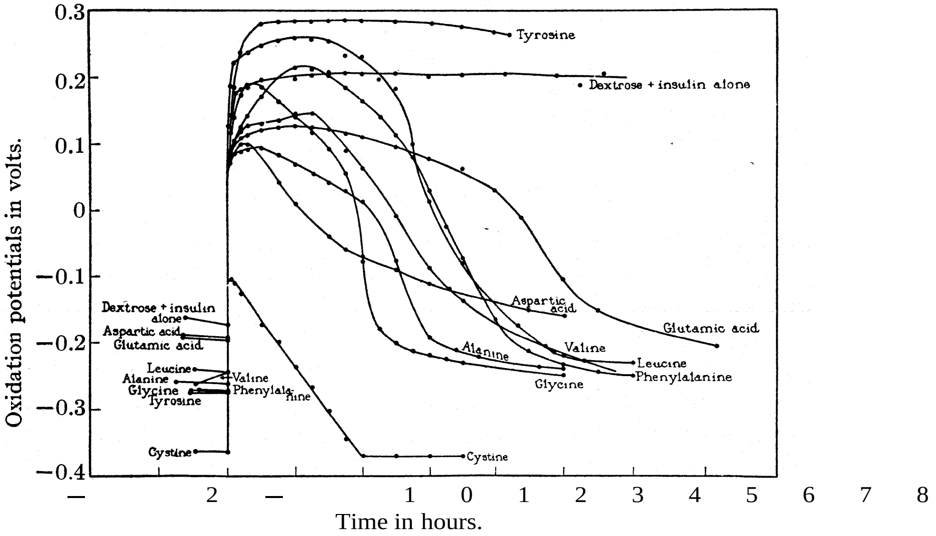

Fig. 4.—Dextrose, insulin and the amino acids.

The effect of insulin on the amino acid catalysis with dextrose is shown in Fig. 4. The action of hydrogen peroxide on dextrose alone seems to be retarded by insulin. This is true to a less extent also in the presence of glutamic acid, glycine and phenylalanine. The catalysis in the presence of cystine and of aspartic acid was somewhat increased. Little change was found for tyrosine, alanine, valine and leucine. The grouping of the amino acids closely according to specific dynamic action seems somewhat lost in the presence of insulin, although complete recovery to reducing conditions, after addition of hydrogen peroxide, is reached again first in the presence of glycine, alanine and phenylalanine, cystine as usual being excepted.

Finally, Fig. 5 shows the results of similar experiments on levulose with insulin and the amino acids. Again the action of hydrogen peroxide on the sugar alone is retarded by the insulin. There is little suggestion of a grouping of the amino acids according to specific dynamic action. The presence of insulin seems to be without much effect on the amino acid catalysis, although most of the curves in Fig. 5 are a little closer together than those in Fig. 2. Again, even when insulin is present, as shown in Figs. 4 and 5, attention is called to the fact that the maximal rate of recovery in all cases is in a region of oxidation intensity approximately between 0.05 and −0.15 volt and that the drop in potentials is abruptly slowed down below −0.2 volt.

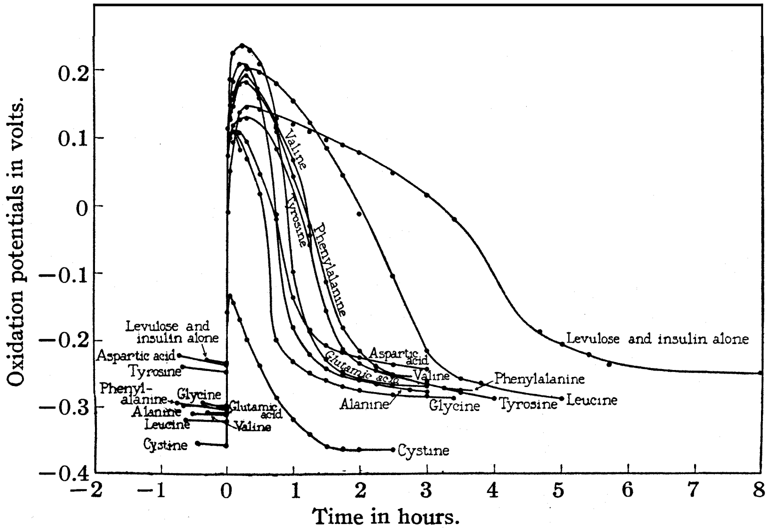

Fig. 5.—**Levulose, insulin and the amino acids.**

Summary

A further study was made on amino acid catalysis of the action of hydrogen peroxide on dextrose and this was continued to include the action on levulose. The sole diierence between the experiments on dextrose alone and those already published is in the faster bubbling of nitrogen gas in these reported at this time. The parallelism between the grouping of the amino acids as catalyzers with dextrose and their grouping according to specific dynamic action is even closer than in the former experiments. Tyrosine alone, which yields slightly higher oxidation potentials than the others, is an exception. At these higher potentials whenever they were obtained in any manner with dextrose alone or with other amino acids it was noticed that the reducing power of the sugar was temporarily paralyzed and the return to more negative potentials much delayed. The connection between amino acid catalysis with levulose and specific dynamic action is much less close than with dextrose.

When insulin was added it was found that the action of hydrogen peroxide on both dextrose alone and levulose alone was retarded. For both sugars insulin had no marked effect on the amino acid catalysis. Some effect, however, was noticed in a smoothing out of the differences between the various amino acids.

Attention is called to the fact that in all cases the maximal voltage change towards a return to reducing conditions takes place in a region approximately between 0.5 and —0.15 volt and that below —0.20 volt the drop is rather quickly stopped. It is hoped in a future paper to discuss the significance of these facts in relation to the mechanism of sugar oxidation in alkaline solutions.

ROCHESTER, MINNESOTA

[CONTRIBUTION RROM THE CHEMICAL LABORATORY OR IOWA STATE COLLEGE]

A STUDY OF THE OPTIMAL CONDITIONS FOR THE PREPARATION OF TERTIARY BUTYLMAGNESIUM CHLORIDE

BY HENRY GILMAN AND E. A. ZOELLNER

RECEIVED JULY 18. 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

It was previously shown by Gilman and McCracken[1] that the yields of the four butylmagnesium bromides decrease in striking fashion with the increasing complexity of branching of alkyl groups, and to such an extent that *tert.*-butylmagnesium bromide gave a yield less than one-fourth of that obtained with n-butylmagnesium bromide. *Tert.*-butyl alcohol is now available at a low cost and the chloride is readily prepared from it in very good yield. Because alkyl chlorides give better yields of RMgCl compounds than the corresponding alkyl bromides[1] a study has been made of several factors affecting the optimal conditions for the preparation of *tert.*-butylmagnesium chloride. As a result of such studies, this tertiary Grignard reagent can now be prepared in quite satisfactory yields.

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[1] Gilman and McCracken, THIS JOURNAL, 45, 2462 **(1923).** Also, Gilman and Kirby, *ibid.*, 48, 1733 (1926) for better yields obtained from chlorides over bromides.

Experimental Part

The apparatus and technique used was essentially that of Gilman and McCracken.[1] The yields were determined quantitatively by the acid titration method of Gilman, Wilkinson, Fishel and Meyers.[2] As an additional check on the yields, several large-sized preparations of trimethylacetic acid were made from *tert.*-butylmagnesium chloride and carbon dioxide. The complex secondary reactions, involving among other things the evolution of considerable isobutylene and isobutane, will be reported later.

Temperature.—Bouveault,[3] who used *tert.*-butylmagnesium chloride in a number of reactions, recommended that the temperature be kept at from 5 to 15° in order to diminish the extent of decomposition evidenced by the evolution of isobutane and isobutylene. We found, on the contrary, that better yields are obtained when the reaction mixture is allowed to reflux as a result of the heat of reaction or is refluxed gently (by use of a water-bath) during the addition of chloride. Solvents other than diethyl ether were not used. In one preparation, the mixture was refluxed after removing aliquots for analysis, and there was practically no change in the concentration of RMgCl compound from that originally present.

Number of Moles of Ether.—Gilman and McCracken[4] have very recently shown that the number of moles of ether required for an optimal yield of Grignard reagent varies with the RX compound. For example, they showed that n-butylmagnesium bromide could be prepared in highest yield with but one mole of ether per mole of halide. With benzylmagnesium chloride 6–7 moles of ether was recommended and with phenylmagnesium bromide 4–5 moles of ether.

With gentle refluxing of the ether solution and a given rate of addition (about 90 drops or 1.4 cc. per minute), the best yield was obtained with about 7–8 moles of ether per mole of chloride.

Rate of Addition of RX Compound.—Gilman and Meyers[5] showed that ethylmagnesium iodide is formed with best yields when the halide in ether is added slowly to the magnesium and ether. This is particularly true in the preparation of *tert.*-butylmagnesium chloride. When the rate of addition is very slow (less than 0.7 cc. per minute) then the yield does not increase but actually decreases to a slight extent. This may be due to the evolved gases (and particularly the circulating hydrogen atmosphere[4,5]) carrying off more of the chloride before it had a chance to reach the magnesium.

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[2] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, 45, 150 (1923). For further data on the reliability of this method and a criticism of another method of analysis see Gilman and Meyers, *Rer. trav. chim.*, 45, 314 (1926).

[3] Bouveault, *Compt. rend.*, 138, 1108 (1904). See, also, Madelung and Volker, *J. prakt. Chem.*, **115,** 24 (1927).

[4] Gilman and McCracken, *Kec. trav. chim.*, 46,463 (1927).

[5] Gilman and Meyers, THIS JOURNAL, **45,** 159 (1923).

The rate of addition in a moderate-sized run is of more significance for ordinary laboratory work than that in the small-sized runs made in the special apparatus. The best yield of trimethylacetic acid, prepared from *tert.*-butylmagnesium chloride and carbon dioxide, was realized when one-half mole of the chloride in 7 moles of ether was added to the magnesium during three hours. This slow addition was at the rate of 2 cc. of halide solution per minute Unquestionably this time can be decreased, for in the small 0.1 mole runs a maximum yield was obtained when the solution was added over a period of two hours.

A possible reason for the better yields when the rate of addition is low is the diminution of a secondary reaction between *tert.*-butylmagnesium chloride and *tert.*-butyl chloride. This finds support in an experiment where the addition of *tert.*-butyl chloride to a solution of *tert.*-butylmagnesium chloride (free from unused magnesium) produced a significant decrease in the quantity of Grignard reagent from that originally present.

Stirring.—In view of the decidedly helpful effect of stirring noted in earlier work, no study was made of this factor and stirring was used throughout all the preparations.[5,6]

Kind of Magnesium.—Gilman and Meyers[5] in their study of the optimal conditions for the preparation of ethylmagnesium iodide used magnesium turnings of three arbitrary grades, coarse, medium and fine. They showed that under a given set of conditions the finer the grade of turnings the higher the yield, but that the factor most affected was the rate of reaction, inasmuch as coarse turnings used over a longer period of reaction gave the same yield as the fine turnings.

No study was made of any reaction rates with *tert.*-butylmagnesium chloride, but there is no question concerning the decided improvement in yield that comes with the use of very fine turnings approximating a powder. This fine material of about 150 mesh was freshly turned and kept in a tightly rubber-stoppered bottle when not in use. A coarser metal of about 30 mesh is also quite satisfactory. Some of the ordinary coarse turnings commercially available for Grignard reactions should not be used for the preparation of *tert.*-butylmagnesium chloride if a finer metal can be had. Fine turnings that give good yields are commercially available in this country.

The finer turnings are recommended largely on the basis of the better yields of trimethylacetic acid from fair-sized preparations of *tert.*-butylmagnesium chloride. The finer turnings, however, would be recommended on the basis of the much smaller runs carried out in the special flasks for estimating quantitatively the yield of RMgX compound. The improvement in yield with the use of finer turnings was more marked in the larger runs.

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[6] Grignard used a shaking device very early in his studies of organomagnesium halides.

The yield of *tert.*-butylmagnesium bromide in one of the smaller-sized runs was 33.1%. Under corresponding conditions the yield of *tert.*-butylmagnesium chloride was 49.71%. Earlier results by Gilman and McCracken under different conditions showed *tert.*-butylmagnesium bromide to be formed in a 20.6% yield.

The maximum yield of *tert.*-butylmagnesium chloride obtained in the several experiments was 58%. In large-sized runs the yield is improved as is evidenced by a 62% yield of trimethylacetic acid from a two and one half mole run of *tert.*-butyl magnesium chloride and carbon dioxide in which fine commercial turnings were used, and by a 69–70% yield when 200 mesh magnesium powder was used.

The authors gratefully acknowledge a liberal supply of *tert.*-butyl alcohol from the Petroleum Chemical Corporation of New York.

Summary

As a result of a study of several factors in the preparation of *tert.*-butylmagnesium chloride it is now possible to 'obtain this Grignard reagent in quite satisfactory yields,

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY NO. 564]

A FURTHER STUDY OF THE INTERACTION OF SULFUR AND PARA-TOLUIDINE IN THE PRESENCE OF LITHARGE: THIO-PARA-TOLUIDINE AND RELATED COMPOUNDS[1]

BY MARSTON TAYLOR BOGERT AND LEONARD SMIDTH[2]

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Introductory

Sulfur dissolves freely in molten p-toluidine to a perfectly clear, transparent, pale yellow solution, which can be heated to about 180° before there is evidence of any reaction, when a slow evolution of hydrogen sulfide begins, gradually increasing as the temperature rises and accompanied by a darkening of the solution, with the ultimate production of dehydrothio-p-toluidine (V), primulines (VI), and other substances.

In the presence of litharge, or other hydrogen sulfide absorbents, however, the reaction begins at much lower temperature (130–145"), as shown first by Merz and Weith,[3] with thio-p-toluidine (III) as the chief product.

This Merz and Weith process has been investigated by Bogert and Mandelbaum,[4] who found that the melt contained both thio- and dithio-

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[1] Presented in abstract before the Division of Dye Chemistry at the Baltimore Meeting of the American Chemical Society, April 8, 1925.

[2] DuPont Fellow at Columbia University for the academic year 1923–1924.

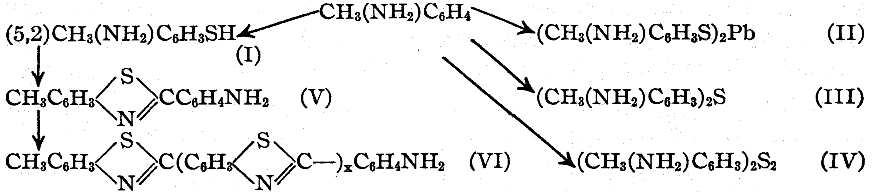
[3] Merz and Weith, *Ber.*, 4, 393 (1871).

[4] Bogert and Mandelbaum, THIS JOURNAL, 45, 3045 (1923).

p-toluidine (IV) and who proved that the sulfur in these products was *ortho* to the amino and *meta* to the methyl groups.

In examining this Merz and Weith fusion further in the experiments which follow, we used one equivalent of sulfur per mole of p-toluidine and, in addition to thio- and dithio-*p*-toluidine, succeeded in isolating from the melt small quantities (less than 1%) of dehydrothio-p-toluidine.

It is our belief that the first product of the action of sulfur upon *p*-toluidine in these fusions is the mercaptan(I), and that this is the progenitor of most of the other products formed, as shown in the following diagram



Ziegler[5] argued many years ago, in discussing the production of dehydrothio-p-toluidine from p-toluidine and sulfur, that since sulfur possesses many properties which recall those of the halogens, it might be expected to substitute either nuclear or side-chain hydrogen depending upon conditions, that high temperature favored side-chain substitution and that the first phase of the reaction, therefore, probably consisted in the formation of p-aminobenzylmercaptan, which condensed with a second mole of p-toluidine to *p*-aminobenzyl-*p*-toluidine, $H_2NC_6H_4CH_2$-$NHC_6H_4CH_3$, and this latter was then transformed into dehydrothio-p-toluidine by the further action of the molten sulfur. The Farbwerke Hoechst[6] subsequently patented the manufacture of dehydrothio-p-toluidine from paminobenzyl-p-toluidine, but no one has yet reported the finding of any p-aminobenzyl-p-toluidine in the dehydrothio-p-toluidine melt, and the experiments of Bogert and Snell[7] demonstrated quite conclusively that the dehydrothio-p-toluidine obtained in following out these patent specifications owed its origin to unchanged p-toluidine remaining in the initial material used. In fact, when toluene itself is heated with sulfur for some time, stilbene is formed in very small amount,[4,8] but no benzyl mercaptan.

Bogert and Mandelbaum[4] separated the products of these Merz and Weith fusions by taking advantage of their different basicities and extracting them successively from a benzene solution of the melt with a series of acids each stronger than its predecessor, p-toluidine thus being removed first, then thio-p-toluidine and finally dithio-*p*-toluidine.

[5] Ziegler, *Ber.*, 23, 2475 (1890).

[6] Farbwerke Hoechst, Ger. pat. 104,230 (May 8, 1899); *Friedlander,* **5,** 83 (1901).

[7] Bogert and Snell, *Color Trade J., 14,* 109 (1924).

[8] Aronstein and van Nierop, *Rec.* trav. *chim.,* 21,450 (1902).

We have now found that the opposite procedure is preferable, namely, the extraction of the melt with excess of mineral acid and the fractional precipitation of the bases by gradual neutralization of this acid solution with ammonia, whereby they are separated in the reverse order, dithio-p-toluidine being thrown down first and *p*-toluidine last.

A perusal of the experimental details of the two processes will make it manifest that the former (fractional extraction with acids) was better adapted to the recovery of the thio-p-toluidine than of the dithio compound, because of the accumulation of tars in the final extracts. For similar reasons, the ammonia precipitation method favored the recovery of the dithio derivative, and incidentally disclosed the fact that the amount of dithio formed was much greater than previously suspected. The two methods thus supplement each other in a very helpful manner and indicate that, based upon the amount of p-toluidine actually consumed in the reaction, the yield of thio-*p*-toluidine is about 25–30%, and of dithio 15–20%.

In the presence of hydrochloric acid, p-toluidine and sulfur interacted to give mainly tar, with but very small amounts of impure dithio-*p*-toluidine, although it has been stated by Hodgson[9] that the latter can be obtained in this way.

Efforts to convert thio-p-toluidine into the 3,9-dimethylphenothiazine,[10] by the action of soda lime, zinc chloride or concd. hydrochloric acid all failed.

Although, as is well known, thio-p-toluidine can be easily diazotized and combined with suitable couplers to form azo dyes, our experiments show that it does not itself function as a coupler for diazotized aromatic bases.

Like Truhlar,[11] we, too, experienced considerable difficulty in getting pure compounds by the application of the diazo reaction to thio-p-toluidine, the products being mostly tars from which we were unable to isolate any crystalline material; but when these tars were oxidized with a mixture of nitric and sulfuric acids, crystalline sulfones were isolated in approximate purity.

In the experiments to obtain a chlorine derivative, the action of concd. hydrochloric acid upon the diazonium chloride gave rise to what appeared to be a mixed ether, whose percentage composition corresponded to the formula $(CH_3C_6H_3ClSC_6H_3CH_3)_2O$, and which may be identical with a product obtained by Truhlar in a similar reaction, described by him as an easily frozen oil containing chlorine and which he was unable to identify.

Attempts to substitute the amino groups by bromine resulted in the

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[9] Hodgson, Brit. pat. 15,466, July **3,** 1911; *C. A.* 7,264 (1913).

[10] Kehrmann, *Ber.,* 39,915 (1906).

[11] Truhlar, *Ber.,* 20, 664 (1887).

replacement of one amino by bromine and the other by hydrogen, as proved by the formation of a monobromo sulfone on oxidation. The di-iodo sulfone, however, was obtained from thio-*p*-toluidine in good yield. All efforts to get a dicyano derivative through the diazo reaction were unavailing.

Experimental Part

Fusion of *p*-Toluidine, Sulfur and Litharge.—These fusions were carried out as described by Bogert and Mandelbaum,[4] except that we found that a slightly lower temperature (130–140°, instead of 140–145°) gave rather better results.

To determine what effect, if any, the litharge had upon p-toluidine in the presence of steam, litharge and the toluidine were added to boiling water and the mixture boiled for some time under a reflux condenser. No change whatever occurred and the p-toluidine crystallized from the colorless aqueous solution as the latter cooled.

A suspension of litharge and sulfur (excess) in boiling water rapidly blackened with formation of lead sulfide and evolution of traces of sulfur dioxide. .

The fusion conditions were varied as follows:

(1) When an intimate mixture of sulfur (1, 1.5 and 3 equivalents) with excess of litharge was added slowly *to* molten p-toluidine (one mole), there was some improvement in the yield of thio-p-toluidine, but more p-toluidine remained unchanged and was recovered.

(2) A mixture of *p*-toluidine (one mole) and excess of litharge was added to molten sulfur (1.5 or 5 equivalents), but the yields of thio-*p*-toluidine were not thereby improved and more tar was formed.

Working up of the Melt.—The cold pulverized melt obtained from *535* g. (5 moles) of p-toluidine, 160 g. (5 equivalents) of sulfur and 800 g. (2.8 moles) of litharge, was extracted repeatedly with 800 cc. portions of 10% hydrochloric acid (or sulfuric) with which it was boiled vigorously for five minutes and the extract filtered hot. The use of stronger acid caused such a copious effervescence of hydrogen sulfide that it was difficult to keep the solution from boiling over.

Each hot filtered 800 cc. acid extract was poured into 1000 cc. of cold water, which precipitated weakly basic resins. The filtrate from these resins was then warmed and treated carefully with ammonium hydroxide solution until the odor of p-toluidine was detected. This precipitated the mono- and dithiotoluidines. Neutralization (with ammonia) of the filtrate from these thiotoluidines caused the separation of practically pure *p*-toluidine.

To recover as much as possible of the mono- and dithiotoluidines present, the thiotoluidine precipitates from the four acid extracts were combined, redissolved in 1800 *g.* of 10% hydrochloric acid and ammonium hydroxide solution added cautiously to this solution, whose temperature was maintained sufficiently high (30–50°) to cause the precipitated dithio compound to separate in a viscous and not a solid form. The color of this viscous precipitate changed as the addition of ammonia proceeded, being yellow at first, then pink and finally red. It was removed mechanically as it accumulated. When all of the crude dithio compound had been precipitated, further addition of ammonia caused the separation of the solid monothio-*p*-toluidine and the precipitate became crystalline. The first portions of this crystalline precipitate were contaminated with some of the dithio derivative and were removed and worked up separately. Further addition of ammonium hydroxide to the filtrate precipitated thio-p-toluidine as a pale yellow solid. The neutralization with ammonia was continued until the odor of p-toluidine was noted or, in the absence of unchanged p-toluidine, until neutrality was reached.

The crude products were purified by a repetition of the process described. In the case of the crude disulfide, its hot dilute acid solution was first poured into sufficient cold water to separate small amounts of basic resins. The filtrate was then precipitated carefully by ammonia as before, any thio-p-toluidine obtained being worked up with the crude thio-p-toluidine fraction. With a little experience the end-points in this separation are easily and quickly noted.

The yields of crude products from one of these fusions were as follows: weakly basic resins (precipitated from acid solution by dilution), 70 g.; dithio-p-toluidine, 80 g., or 17%; monothio, 121 g. or 26%; p-toluidine recovered, 167 g. The yields of mono- and dithiotoluidine are calculated on the basis of the net amount of p-toluidine consumed in the operation.

From one of these fusions, conducted at 140–145°, 20 g. of the resinous products precipitated by dilution of the acid solution was extracted repeatedly with large volumes of boiling water and yielded a total of 0.96 g. of impure dehydrothio-*p*-toluidine (m. p. 186°), or less than 1% of that calculated from the initial materials. When the fusion temperatures were below 140°, only traces of this compound could be found in the melts. No trithio-p-toluidine was isolated from the melt, nor any compounds other than those already mentioned.

The Interaction of *p*-Toluidine and Sulfur in the Presence of Concentrated Hydrochloric Acid.—Hodgson[12] reports a nearly theoretical yield of trithio-o-toluidine when he heated together o-toluidine, hydrochloric acid and sulfur for two to three hours at 185–190°, and similar results in the case of aniline.[13] We repeated this work with o-toluidine and obtained excellent yields of the trithio-o-toluidine, melting at 225° (uncorr.). Hodgson gives the melting-point of the pure product as 226–227° (uncorr.).

In his original patent,[9] Hodgson states that p-toluidine, under similar conditions, gives a dithio derivative, and hence we carried out various experiments with p-toluidine, hydrochloric acid and sulfur, following the Hodgson process, but succeeded in obtaining only very small amounts of impure dithio-p-toluidine, together with some unchanged p-toluidine and a large amount of tar. The difference in the behavior of the two toluidines when treated in exactly the same way was striking.

Thio-*p*-toluidine, as prepared by the process described, was usually colorless and melted above 100°. Its further purification was accomplished by crystallization from diluted alcohol; or the solution in hot 10% hydrochloric acid, after precipitation of any disulfide (unless the disulfide is precipitated first by ammonia, the addition of concd. hydrochloric acid tends to throw down its hydrochloride as well as that of the monosufide), was treated with concd. hydrochloric acid until precipitation began, when the solution was allowed to cool and the hydrochloride separated in colorless, feathery

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[12] Hodgson, J. *Chem. Soc.*, 101, 1693 (1912).

[13] Hodgson and Dix, *ibid.*, 105,952 (1914).

needles, which were dissolved in boiling water and the free base precipitated by neutralization with ammonia. A single crystallization from diluted alcohol than gave colorless leaves, m. p. 103–104°, in agreement with the literature.

Heated above its melting-point, it was unchanged at 150°; at 180–190°, small amounts of ammonia were given off; at 200°, ammonia and hydrogen sulfide; at 205–210°, ammonia, hydrogen sulfide and p-toluidine (identified by its odor, its melting point and the melting point of its aceto derivative). The residue was brown and amorphous, and its benzene solution was strongly fluorescent.

No change was detected when thio-p-toluidine and concd. hydrochloric (or 25% sulfuric) acid were heated together for six hours at 200°, except the formation of some p-toluidine. When fused for several hours with sulfur, thio-p-toluidine was not decomposed, nor could any dehydrothio-p-toluidine be isolated from the melt.

A mixture of 71 g. of thio-p-toluidine (m. p. 103–104°) and 19 g. of sulfur was heated at 140–150° and 65 g. of litharge added gradually during eight hours. By extracting the cooled and pulverized melt with hydrochloric acid, 60 g. of crude thio-*p*-toluidine (that is, 84.5% of the original amount) was recovered, together with a small quantity of acid-soluble tars. The thio-p-toluidine formed in the p-toluidine-sulfur fusion, therefore, is not very rapidly or extensively decomposed by the litharge and sulfur added.

In acid solution, thio-p-toluidine refused to couple with diazotized sulfanilic acid. On the other hand, azo dyes are readily produced by uniting diazotized thiotoluidine with suitable couplers, and were patented long ago by Dahl & Co.[14] We verified this by coupling the diazotized thiotoluidine with H-acid in sodium carbonate solution and obtained an azo dye which gave deep purple shades on wool, fast to light, acids, alkali or soap.

Diaceto Derivative.—This was prepared as recorded by Bogert and Mandelbaum[4] and corresponded in appearance and melting point with their description. It was subjected to some further tests, with the following results.

To attempted bromination, nitration or sulfonation, it proved very resistant, decomposition generally occurring before the desired substitution could be realized. At laboratory temperature, a mixture of concd. nitric and sulfuric acids (75:30) oxidized it to the corresponding diaceto sulfone; this proved to be a convenient way of preparing the latter compound, instead of the permanganate method employed by Bogert and Mandelbaum.

Bis(2-Acetamino-5-methylphenyl) Sulfoxide, $(CH_3CONHC_6H_3(CH_3))_2SO$.—Attempts to oxidize thio-p-toluidine in acetone solution with hydrogen dioxide, by the method of Gazdar and Smiles,[15] resulted in tar and unchanged initial material, but no appreciable yield of sulfoxide. Hinsberg,[16] however, has found that aceto derivatives often can be used advantageously for such oxidations and we followed this lead successfully.

To a well cooled solution of 5 g. of thio-*p*-toluidine in 6 cc. of acetic anhydride, there were added 20 cc. of glacial acetic acid and 2 cc. of 30% hydrogen dioxide ("Superoxole"). After standing for twelve hours at room temperature, the solution was poured into a large' volume of water and the acid neutralized with ammonia. The precipitate crystallized from alcohol in colorless hexagonal plates, m. p. 212° (corr.); yield, 2 g. or 28%.

Anal. Calcd. for $C_{18}H_{20}O_3N_2S$: C, 62.75; H, 5.87. Found: C, 62.79; H, 5.89.

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[14] Dahl & Co., Ger. pat. 34,299; *Friedlander,* 1, 534 (1885); Brit. pat. 14,232 of 1885.

[15] Gazdar and Smiles, J. *Chem. Soc.*, 93, 1833 (1908).

[16] Hinsberg, *Ber.*, 41, 2836 (1808).

Bis(2-Chloro-5-methylphenyl) Sulfone.—A solution of 5 g. of thio-p-toluidine in 80 cc. of water and 12 cc. of concd. hydrochloric acid was diazotized at 0° with an aqueous solution of 3.3 g. of sodium nitrite and 6 g. of copper powder was added. After standing for an hour, the mixture was heated at 100° until the evolution of gas ceased. The tarry precipitate was oxidized as described beyond for the analogous iodo derivative. The product was a pale brown, amorphous solid which decomposed slowly above 95°; yield, 2.1 g., or 33%. It was readily soluble in chloroform or acetone, less readily in benzene and practically insoluble in alcohol.

Anal. Calcd. for $C_{14}H_{12}O_2Cl_2S$: C, 53.32; H, 3.84. Found: C, 53.91; H, 3.46.

Bis(2-Chloro-5,5′-dimethylphenylsulfide)-2,2′-Oxide, $(CH_3C_6H_3ClSC_6H_3CH_3)_2O$.—A solution of 24.5 g. of thio-p-toluidine in 100 cc. of concd. hydrochloric acid and 150 cc. of water was diazotized at 0° (some of the thiotoluidine hydrochloride tends to separate as the temperature of the solution falls) by a solution of 15 g. of sodium nitrite in 75 cc. of water. After standing for thirty minutes at 0°, the solution was poured into 450 cc. of concd. hydrochloric acid and the mixture left overnight at room temperature. Gas was evolved slowly. The solution was heated gradually to boiling. A black oil soon separated and the reaction appeared to be at an end. The oil was removed, washed with strong aqueous caustic alkali, then with water, after which it was distilled at 80 mm. pressure and a fraction collected at 265° which formed a colorless oil that darkened gradually on standing; yield, 15 g. or 59%.

Anal. Calcd. for $C_{28}H_{24}OCl_2S_2$: C, 65.75; H, 4.69; S, 12 52; Cl, 13.90. Found: C, 65.66; H, 5.07; S, 12.81; Cl, 14.42.

This compound was insoluble in strong caustic alkali solutions. A distinctive and striking property was the deep blue color it gave when treated with concd. sulfuric acid. Oxidation with acid permanganate failed to yield a crystalline sulfone, while strong oxidation with nitric acid broke down the molecule to unidentified products soluble in the diluted acid.

2-Bromo-5,5′-dimethylphenyl Sulfone, $CH_3BrC_6H_3SO_2C_6H_4CH_3$.—Ice was added to 17 g. of concd. sulfuric acid until the temperature was reduced to 0°, when 5 g. of thio-p-toluidine was stirred in and the solution diazotized with an aqueous solution of 3 g. of sodium nitrite. To this diazo solution, there were added 30 g. of potassium bromide and 10 g. of copper powder, and the rest of the process followed that described for the analogous chloro and iodo derivatives. The product was a brownish, amorphous solid which decomposed slowly at about 69–72°; yield, 1.6 g. or 24%. It dissolved easily in chloroform, acetone or benzene, less freely in ether, only slightly in carbon tetrachloride and was practically insoluble in alcohol.

Anal. Calcd. for $C_{14}H_{13}O_2BrS$: C, 51.69; H, 4.00. Found: C, 52.16; H, 3.64.

These figures indicate that one only of the two original amino groups of thio-*p*-toluidine was replaced by bromine, while the other was substituted by hydrogen, but not enough pure material was left to check this by determining also the percentage of bromine present.

Bis(2-Iodo-5-methylphenyl) Sulfone.—To a diazo solution prepared from 5 g. of thio-p-toluidine and the requisite amounts of hydrochloric acid and sodium nitrite, there was run in slowly a cold saturated aqueous solution of 12 g. of potassium iodide. When the first rapid evolution of nitrogen subsided, the mixture was warmed at 100" until no more gas was given off. The black, viscous precipitate was collected, washed with water, dissolved in glacial acetic acid and sufficient potassium acid sulfite added to convert any free iodine into potassium iodide. When this solution was poured into water, a yellow, gummy precipitate separated. This was added in small quantities to a mixture of concd. nitric (15 cc.) and sulfuric (6 cc.) acids and the mixture warmed until a copious evolution of nitrogen oxides occurred. The oxidation was completed very quickly. The acid liquid was poured into water, the precipitate removed, warmed with strong caustic soda solution, the undissolved material dissolved in boiling glacial acetic acid, the solution decolorized and poured into water. The precipitate was collected, washed with hot alcohol and subjected to further purification by re-solution in glacial acetic acid, decolorization and reprecipitation by dilution. This precipitate, when washed with water and alcohol and dried, appeared as a pale brownish, amorphous solid which began to decompose in the neighborhood of 82°; yield, **4.3** g. or 42%. **It** dissolved freely in chloroform, acetone or carbon disulfide, less readily in benzene, but slightly in ether and was practically insoluble in alcohol or carbon tetrachloride.

Anal. Calcd. for $C_{14}H_{12}O_2I_2S$: C, **33.73; H, 2.43;** S, **6 44;** I, **50.96.** Found: C, **33.14; H, 2.25;** S, **6.30;** I, **50.25.**

Dithio-*p*-toluidine.—The crude product obtained in the process described was purified further by dissolving it in hot alcohol, adding water or, better, ammonium hydroxide solution, to incipient clouding and allowing the solution to cool. The yellow, lustrous leaflets obtained, melted at **88–89",** in accord with the literature.

Hodgson[17] reports that when dithio-aniline (10 g.) is boiled for eight hours with dry aniline (20.4 g.), the yield of monothio-aniline is practically equal to that calculated, but that the presence of water retards this reaction and may inhibit it entirely. From this latter statement, it would seem unlikely that much thio-aniline could be formed from the dithio during an aniline-sulfur-litharge fusion, for steam is given off continuously during this reaction due to the gradual addition of the litharge. Yet, K. A. Hofmann[18] states that he obtained thio-aniline by heating an aniline solution of dithio-aniline for one and one-half hours at 170–180°, with the gradual addition of somewhat more than one mole of litharge, and Hodgson,[19] who repeated Hofmann's experiments, isolated both o,o - and o,p -monothio-anilines from the melt.

It seemed desirable, therefore, to ascertain the behavior of dithio-p-toluidine under similar conditions, and the following experiments record the results.

A mixture of 6 g. of dithio-*p*-toluidine (carefully purified and free from the monothiotoluidine) and **20** g. of p-toluidine was heated for eight hours at 140–150**'**, while **10** g. of litharge was added gradually to the melt. From this melt there were recovered **5.1** g. of the original disulfide and **18** g. of p-toluidine, but no thio-*p*-toluidine. Increase in the fusion temperature to 165° did not alter this result materially, except that at the higher temperature some tar was formed.

To determine the effect of sulfur and litharge upon the disulfide, 9 g. of the latter was heated with **4** g. of sulfur for eight hours at 160–165°, while **10** g. of litharge was added gradually. Most of the initial disulfide was recovered from the melt unchanged, together with about **0.7** g. of acid-soluble resins.

Like the monosulfide, this disulfide may be used for the preparation of azo dyes.[9,20]

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[17] Hodgson, **J.** *Chem. Soc.*, *125,* **1856** (1924).

[18] **K. A.** Hofmann, *Ber.,* **27,2810 (1894).**

[19] Hodgson, **J.** *Soc. Dyers Colourists, 40,* **333 (1924).**

[20] British Dyestuffs Corp. Ltd. and H. H. Hodgson, Brit. pat. **235,334** of April **1, 1924.**

Diazotized and coupled with H-acid in sodium carbonate solution, it gave a dye which produced purplish shades on wool, lighter in tone than the corresponding dye from the monosulfide, but resembling it in its fastness to light, acids, alkali and soap.

PICRATE.—Equal moles of the disulfide and picric acid were mixed in hot benzene solution and the picrate was crystallized as the solution cooled. Recrystallized from benzene it formed long, silky, yellow needles

The DIACETO DERIVATIVE has been described by Bogert and Mandelbaum.[4] When it was oxidized either with nitric acid or with acid permanganate, the product appeared to be a sulfonic acid. We failed to obtain either a sulfoxide or a sulfone.

2-Amino-5-methylphenyl Mercaptan, $CH_3(NH_2)C_6H_3SH$.—Reduction of dithio-p-toluidine by zinc dust and acetic acid, or by tin and hydrochloric acid, gave the zinc or tin salts of the mercaptan, from which the mercaptan itself was liberated by the action of hydrogen sulfide.

In a typical experiment, **10** g. of the crude disulfide was dissolved in **200** cc. of boiling glacial acetic acid, 20 g. of zinc dust added gradually and the mixture refluxed for an hour. Longer boiling of the acetic acid solution proved detrimental to both yield and purity of the product. It was then filtered hot, the filtrate diluted with **2.5** volumes of water and allowed to stand for ten to fifteen minutes. On longer standing, impurities present in a crude initial disulfide are also likely to separate. The white, flocculent precipitate of zinc salt was collected, washed with water, then with a little ether and dried at **110°**; yield, 5.6 g. or 45%.

Anal. **0.9824** g. ignited gave **0.2319** g. of ZnO, or **23.60%**: calcd., **23.82%**.

Liberated from its zinc or tin salts by hydrogen sulfide, the mercaptan gradually oxidized in the air to the disulfide.

Summary

1. A further study has been made of the Merz and Weith reaction for the production of thio-p-toluidine from *p*-toluidine, sulfur and litharge, and a new method of separating the products worked out which depends upon their fractional precipitation from acid solution by ammonia.

2. Various experiments are recorded which throw light upon the probable mechanism of the reaction, and indicate that the action of sulfur upon *p*-toluidine follows a somewhat different course from that of sulfur upon either aniline or o-toluidine.

3. Additional properties and reactions of both thio- and dithio-p-toluidine are described, including their conversion into various derivatives.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

AROMATIC PROPERTIES OF SOME ALIPHATIC COMPOUNDS LOCAL ANESTHETICS DERIVED FROM ALIPHATIC CARBOXYLIC ACIDS

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Introduction

The differences between aromatic and corresponding aliphatic compounds are largely of degree and not of kind. There are probably no rigidly exclusive aromatic characteristics. Functional groups that have the so-called aromatic properties are almost invariably attached to a tertiary carbon atom that has some degree or other of unsaturation. A fair basis of comparison would restrict correlation to aliphatic compounds that have functional groups of a related type. When this condition is met, in part or in whole, one observes that practically all the so-called distinctive aromatic properties are shown by varied aliphatic compounds.[1]

The present work extends such correlation to include the comparative physiological action of some aromatic compounds with related aliphatic types. Previously, Gilman and Pickens[2] showed a correlation, based on physiological action, between some aromatic heterocyclic types (furan, thiophene and pyrrole) and benzene. For comparative purposes the same physiological action, namely, local anesthetic action, has been studied. It has been found that the diethylamino-ethyl esters of carboxylic acids (where the carboxyl group is attached to an ***unsaturated*** carbon atom, $RCH{=}CHCO_2CH_2CH_2N(C_2H_5)_2$) show a distinct, although small, local anesthetic action. Where the same grouping is attached to a saturated carbon atom there is no local anesthetic action.

For comparative purposes it is interesting to observe that when the unsaturated acid contains also a phenyl radical, as in cinnamic acid, the anesthetic action is increased. Also, the cinnamic acid ester of diethylaminopropyl alcohol ("Apothesin") is distinctly active. Its high potency is no doubt partly due to the introduction of the phenyl radical into the acrylic acid and partly to the fact that the amino-alcohol part of the molecule contains an additional carbon atom.

Experimental Part

The hydrochlorides of the diethylamino-ethyl esters were prepared by a standard technique involving the interaction of the acid chloride

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[1] Space does not permit of reference to the many works in this field. A general and leading account of some such correlations is to be found in Johnson and Hahn's translation of Henrich's "Theories of Organic Chemistry," John Wiley and Sons, Inc., New York, 1922, in particular see pages 182–183, 232 and 234–235

[2] Gilman and Pickens, THIS JOURNAL, 47,245 (1925).

with diethylamino-ethanol in an inert medium, generally benzene or ether.

Diethylamino-ethyl **Acrylate** Hydrochloride, $CH_2{=}CHCO_2CH_2CH_2N(C_2H_5)_2.HCl$.—Eight g. or **0.088** mole of acrylic acid chloride[3] in **50** cc. of dry benzene was added dropwise to **11** g. or **0.094** mole of β-diethylamino-ethanol in **50** cc. of benzene. The hygroscopic hydrochloride of diethylamino-ethyl acrylate melted at 93° when crystallized from benzene.

Anal. Calcd. for $C_9H_{18}O_2NCl$: Cl, **17.07;** N, **6.70.** Found: Cl, **16.89, 16.53;** N, **6.30.**

Preliminary to the above synthesis, β-chloro-ethyl α,β-dibromopropionate, $CH_2BrCHBrCO_2CH_2CH_2Cl$, was prepared by passing hydrogen chloride into a mixture of α,β-dibromopropionic acid and ethylene chlorohydrin. The yield of ester boiling at 153° **(20** mm.) was **92.9%;** n^{30} = **1.9080;** d_4^{20} = **1.5241.**

Anal. Calcd. for $C_5H_7O_2Br_2Cl$: Br, 54.31; Cl, **12.03.** Found: Br, **54.20;** Cl, **12.02.**

Diethylamino-ethyl **β,β-Dimethylacrylate** Hydrochloride, $(CH_3)_2C{=}CHCO_2CH_2CH_2N(C_2H_5)_2.HCl$.—This compound was prepared from dimethylacrylic acid chloride and diethylamino-ethanol in ether. When crystallized from acetone it melted at 128.5–130°.

Anal. Calcd. for $C_{11}H_{22}O_2NCl$: Cl, **15.07.** Found: Cl, **15.2.**

Diethylamino-ethyl Trichloro-acetate Hydrochloride, $CCl_3CO_2CH_2CH_2N(C_2H_5)_2.HCl$.—The same general conditions were followed here as in the preparation of the β,β-dimethylacrylate ester hydrochloride. The compound melted at 144–145°.

Anal. Calcd. for $C_8H_{15}O_2NCl_4$: N, **4.68.** Found: N, **4.76.**

Diethylamino-ethyl Acetate, $CH_3CO_2CH_2CH_2N(C_2H_5)_2.HCl$, melted at 116–117°.

Anal. Calcd. for $C_8H_{18}O_2NCl$: Cl, **18.12.** Found: Cl, **18.09, 18.14.**

Some preliminary reactions were carried out between diethylamino-ethanol and the acid chlorides of fumaric and monochloro-acetic acids. From these the hydrochloride of 8-diethylamino-ethanol was obtained.

Pharmacological Tests

The authors are indebted to Dr. Oliver Kamm of Parke, Davis and Company of Detroit for the results of the pharmacological tests. The method of testing was that described earlier.[2] Cocaine was selected arbitrarily as a standard and given a weight of 10. On a scale of this kind, the relative and rather approximate ratings of the hydrochlorides are as follows: diethylamino-ethyl dimethylacrylate is 1; diethylamino-ethyl acrylate is also 1; diethylamino-ethyl trichloro-acetate is slightly less than 1; and diethylamino-ethyl acetate is zero. "Apothesin," diethylaminopropyl cinnamate, has a rating of approximately 8 on this basis.

Diethylamino-ethyl trichloro-acetate was selected in this study because trichloro-acetic acid has, among other properties, a conductivity that places it nearer to aromatic compounds than acetic acid.

It is interesting to note that the comparative effectiveness of the diethylamino-ethyl esters of acrylic and dimethylacrylic acids places them

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[3] Prepared according to direction.; of Moureu, *Ann. chim. phys.*, *[7]*2, 161 (1894).

not far from two of the aromatic types previously reported,[2] namely, diethylamino-ethyl 2-thiophenecarboxylate (with a rating of 1) and diethylamino-ethyl 2-furancarboxylate (with a rating of less than 1).

Summary

A study of the local anesthetic action of some diethylamino-ethyl esters of aliphatic carboxylic acids shows that the chemical correlation of aromatic compounds with some related aliphatic compounds can be extended to include physiological action.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE TAUTOMERISM OF HYDROXY QUINONES

BY LOUIS F. FIESER

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It is the purpose of this paper to apply to the problem named in the title certain of the principles governing chemical equilibria, and to present the results of experiments which were carried out with the view of testing and applying this theoretical treatment of the subject.

1. The General Theory

Hydroxynaphthoquinone is typical of the compounds under consideration. While only one form of the substance is known in the solid state,[1] it is necessary to recognize the presence of two tautomeric forms in its solutions in order to account for the course of the hydrolysis of 2-alkoxy-1,4-naphthoquinones and 4-alkoxy-1,2-naphthoquinones, for a single solid substance results in each case.[2] Among the reactions which demonstrate the presence of hydroxy-a-naphthoquinone in the equilibrium mixture is that with diazomethane,[2] while the ready, reversible reaction of hydroxynaphthoquinone with sodium bisulfite must involve a β-naphthoquinone derivative. Thus these tautomers, which may be referred to as the α and β forms of hydroxynaphthoquinone, must be present in all solutions of the substance and the constant of the tautomeric equilibrium may be defined by the following equation

$$K = [\alpha\text{-Form}]/[\beta\text{-Form}] \qquad (1)$$

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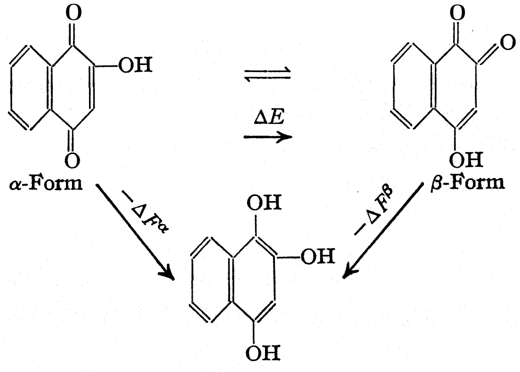
[1] Miller's statement to the contrary, *J. Russ. Phys.-Chem. Soc.*, **43**, 440 (1911), must be discounted. It is possible that the change in his sample on storage and the variation of the point of decomposition of this substance are both due in part to a reaction of the material with glass. Some of the samples which Miller prepared by different methods undoubtedly contained impurities. Dr. Samuel C. Hooker has informed me that, by following with the microscope the crystallization of a red sample of this quinone, he found the red color to be due to the presence of impurities removed only after numerous crystallizations.

[2] Fieser, THIS JOURNAL, 48, 2922 (1926).

In order to obtain a method of estimating the magnitude of K, use may be made of the fact that the tautomers have a common reduction product.



For the purpose of the following theoretical treatment it is convenient to postulate the free energy changes involved in the conversion of one tautomeric quinone into the other and in the conversion of each quinone into the common hydroquinone. It should be clearly realized that it is not possible at the present time to determine directly any of these quantities. There remains, however, the possibility of developing a method of reasoning by analogy which will serve to give an approximate evaluation of the tautomeric equilibrium constant, and it is with this end in view that a thermodynamic analysis of the problem will be presented. The free energy change in the conversion of the a-form at unit concentration in a given solvent into the β-form at the same concentration, AF. is equal to the free energy of reduction of the a-form $(-AF^{a})$ minus the free energy of oxidation of the reductant to the β-form $(-\Delta F^{\beta})$

$$\begin{array}{llll} & \text{a-Form} + 2\text{H} & = \text{Reductant} & -\Delta F^{\alpha} \\ & \text{Reductant} & = \beta\text{-Form} + 2\text{H} & + \Delta F^{\beta} \\ \hline \text{(Adding)} & \text{a-Form} & = \beta\text{-Form} & -\Delta F^{\alpha} + \Delta F^{\beta} \\ \textbf{(Or)} & & \Delta F = -\Delta F^{\alpha} + \Delta F^{\beta} & \end{array} \qquad (2)$$

The free energy changes in the reduction of the two quinones are conveniently expressed in terms of the normal reduction potentials of the tautomers in the solvent in question, E_0^{α} and E_0^{β}, since $-$ A F = nFE_0. Making these changes, and substituting for A F the expression RT ln K, Equation 2 becomes, for 25°

$$\log K = (E_0^{\beta} - E_0^{\alpha})/0.0296 \qquad (3)$$

There is thus a simple relationship between the equilibrium constant of the tautomerization and the difference in the normal reduction potentials of the two tautomers. That form which has the lower reduction potential will predominate; thus, if E_0^{α} is less than E_0^{β}, K will be greater than one and [α-Form] > [β-Form]. This principle is novel to the organic chemist only in its quantitative aspects. Dimroth for example in assigning structures to certain hydroxynaphthoquinone derivatives arbitrarily wrote the α-naphthoquinone formulas because, as he says, "in general, para quinones are more stable than ortho quinones," ("im allgemein Parachinone stabiler sind als Orthochinone.")[3] The first statement of the idea was probably that of Kehrmann,[4] who applied it to a study of the structure of the azines. Beschke[5] presented evidence in support of his conception that, if a given substance can give rise to two different quinones on oxidation, the quinone of lower oxidizing power will result. The presence of a common reduction product is not, however, essential for the interconversion of the tautomers. To be sure, Equation **3** was derived with the use of normal potentials, that is, electrode potentials of mixtures containing equivalent quantities of the oxidant and reductant, but it applies equally well to the "pure solutions" of the quinones.

Before considering extensions of Equation **3,** it will be well to demonstrate how this equation can be applied to the solution of practical problems. The isolation of the tautomeric forms of an hydroxy quinone has not yet been accomplished, and it is not likely that potential measurements could be carried out with such substances without the occurrence of a tautomeric change. However, although the terms E_0^β and E_0^α cannot be determined directly, it is possible in many instances to estimate these potentials, or the difference between them, from the known values of compounds of related structure. The soundness of this process of reasoning depends upon the nature of the analogy of which use is made in any particular case. In the following pages, in which an attempt has been made to determine the approximate composition of the equilibrium mixtures of certain hypothetical tautomer pairs, various methods of predicting the potentials of the tautomers have been employed, and each case should be judged on its own merits.

2. Hydroxynaphthoquinone

It will be seen from Equation **3** that all that is required for an evaluation of the equilibrium constant, K, is a knowledge of the difference between the potentials of the tautomers. Although there is at present no way of predicting the potentials of the two possible forms of hydroxynaphthoquinone, it is possible to decide which form would have the higher potential and to estimate the magnitude of the difference between the two values from a knowledge of the potentials of the ethers, I and II. While the potentials of these ethers may not be the same as those of the corresponding hydroxy compounds, it is highly probable that the difference

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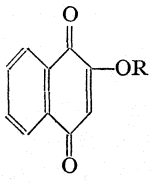
[3] Dimroth and Kerkovius, Ann., 399, 36 (1913).

[4] Kehrmann, *Ber.*, 31, 977 (1898).

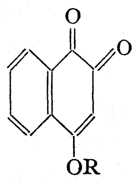
[5] Beschke and Diehm, Ann., 384, 173 (1911).

between the two values is approximately the same as the difference between the potentials of the two tautomers.

Data which will permit a prediction of the magnitude of this difference are furnished by the results of e. m. f. measurements with a series of ethers of the type of I and II (Table I). In order to prevent the hydrolysis of the o-quinone ethers it was necessary to employ a neutral solution, while the insolubility of some of the ethers in water necessitated the use of an alcoholic solution. The solvent which was consequently employed (see table) did not permit the use of the ordinary reducing agents and so the quinones were reduced with hydrogen and a catalyst and the hydroquinones titrated electrometrically with potassium ferricyanide dissolved in the same solvent. The normal reduction potential (E_0) is equal to the e. m. f. of the cell: Pt | Solvent A, Quinone, Hydroquinone | Solvent A | H_2 | Pt, at the point of half-reduction. Under ΔE_1 and ΔE_2 are given the average differences between E_0 and the potential at 20% and at 80% oxidation. The theoretical value is 17.8 mv.



I



II

TABLE I

REDUCTION POTENTIALS AT 25°

Solvent: 37% alcohol, 0.047 M in KH_2PO_4 and 0.047 M in Na_2HPO_4

No.	Alkyl group	E_0, v.				ΔE_1, mv.	ΔE_2, mv.	E_0 (av.), v.
		A. 2-Alkoxy-1,4-naphthoquinones						
1	**Methyl**	0.353	0.354			19.2	19 3	0.353
2	**Ethyl**	.352	.354			18.0	18 0	.353
3	**n-Propyl**	.353	.353	0.351	0.350	20.1	19.7	.352
4	*n*-Butyl	.351	.352			19 5	19 2	.351
		B. 4-Alkoxy-1,2-naphthoquinones						
5	**Methyl**	0.433	0.433	0.433		20 1	18 3	,433
6	**Ethyl**	.430	.430			19.1	18 0	.430
7	**n-Propyl**	.430	.430			18 0	19 9	.430
8	*iso*Propyl	.426	.426			20.4	181	.426
9	**n-Butyl**	.422	.423	.421		21.2	18.9	.422

Table I indicates that there is a slight decrease in reduction potential with increasing size of the alkoxyl group. Since of these groups the methoxyl is the most similar in structure to the hydroxyl group, the difference in the potentials of the two methyl ethers may be taken as a measure of the difference in potential of the two tautomerie hydroxy compounds, though the result is much the same if any other pair of ethers is selected. Substituting the value $E_0^\beta - E_0^\alpha = 0.080$ v. in Equation **3,** it is found that for hydroxynaphthoquinone K = 502. This means that in the solvent in question only 0.2% of the β-form is present in the equilibrium mixture. From the facts known concerning the variation of quinone reduction potentials with changes in temperature and in solvent (at constant P_H),[6] it can be said that the composition of the equilibrium mixture will be changed to an inappreciable extent by such changes in the conditions. These conclusions are in agreement with all of the known properties of the substance in question and this theoretical treatment finds particular support in the course of the hydrolysis of ethers of the β-form.[2]

3. Naphthopurpurin

There are two structures, IIIa and IIIb, which represent the possible tautomeric forms of naphthopurpurin.[7] It is not difficult to predict what the reduction potential of a pure substance possessing the structure of IIIa would be, for this differs from naphthazarin, IV, only in having an extra hydroxyl group, and the effect of such a group on the potential of a quinone is easily determined. By the use of certain analogies, a prediction can also be made concerning the potential of IIIb. Thus an idea can be gained of the relative values of E_0 for the two tautomers and, consequently, of the equilibrium constant.

The potential of naphthopurpurin itself can be determined by direct measurement; but this measurement furnishes no indication of the possible existence of two tautomers in the solution. The value found will depend upon the potentials and the concentrations of the tautomers, but there is no way of deducing from this value, taken by itself, the composition of the mixture or the potential of either tautomer. However, if on reasoning by analogy it can be shown, for example, that IIIa would have a much lower potential than IIIb, there is reason to believe that in a solution of naphthopurpurin IIIa predominates to the practical exclusion of IIIb. In this event, the experimentally determined potential of naphthopurpurin would represent the potential of tautomer IIIa in practically pure form, and a comparison of the experimental value with the value predicted for IIIa would furnish a check on the validity of conclusions drawn solely from a consideration of the potentials predicted for the tautomers.

The potential of naphthopurpurin, together with data required for the predictions indicated, is given in Table II. While compound No.

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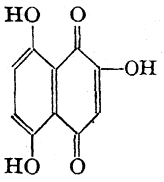
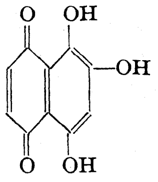
[6] Conant and Fieser, THIS JOURNAL, 44, 2480 (1922).

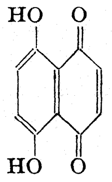
[7] In view of the definite chemical and electrochemical evidence pointing to the P-quinonoid structure for hydroxynaphthoquinone, it is not necessary to consider an o-quinone formula for naphthopurpurin or for the dihydroxyquinone, V, below.



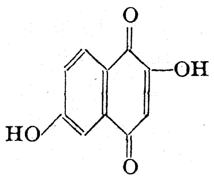
IIIa



IIIb



IV[8]



V

TABLE II

REDUCTION POTENTIALS AT 25°

Solvent: 50% alcohol, 0.1 N in HCl and 0.2 N in LiCl.

No.		E_0, v.				ΔE_1, mv.	ΔE_2, mv.	E_0 (av.), v.
10	Naphthopurpurin (III)	0 243	0 243	0 244	0 243	21.8	20.7	0.243
11	Naphthazarin (IV)	.362	361	359	362	20.2	20 9	361
12	2,6-Dihydroxy-1,4-naphthoquinone (V)	.303	.304	.302		18.1	18.6	303

12 was titrated electrometrically with titanous chloride, this reagent could not be employed with the other quinones because highly colored precipitates were formed. In these cases the hydroquinone solutions were prepared by catalytic hydrogenation and titrated with a solution of benzoquinone.

In order to estimate the potential of IIIa, the potentials of 2-hydroxy-1,4-naphthoquinone (E_0 = 0.356 v.),[9] of naphthazarin (IV), and of a-naphthoquinone (E_0 = 0.483 v.)[9] under comparable conditions are re-required. Thus E_0 (IIIa) = 0.356 − (0.483 − 0.361) = 0.234 v. For a prediction concerning IIIb, it is necessary to know the potential of naphthazarin (IV) and the effect of a hydroxyl group in the β position in the benzoid ring. The latter information is furnished by a comparison of hydroxynaphthoquinone with its 6-hydroxy derivative, V. Then E_0 (IIIb) = 0.361 − (0.356 − 0.303) = 0.308 v. Since the potential predicted for IIIa is 0.074 v. lower than the value estimated for IIIb, it is reasonable to suppose that IIIa is the predominant tautomer. Assuming the accuracy of these predictions, the equilibrium constant for naphthopurpurin calculated from Equation 3 is 157, whence about 0.4% of the less stable tautomer, IIIb, is present at equilibrium.

If this reasoning is correct, the experimentally determined value for naphthopurpurin must be very close to the actual potential of IIIa. The value predicted for IIIa, 0.234 v., agrees just as closely with the value found, 0.243 v., as could be expected. It is not yet possible to calculate potentials with greater accuracy than this. Thus, from the potentials of 4-ethoxy- and 4-(n-propoxy)-1,2-naphthoquinone (Table I), one would expect the n-butyl derivative to have a potential of 0.430 v.; but the actual value is 0.422 v. The above discrepancy of 0.009 v. is thus of little sig-

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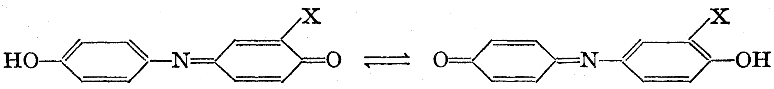
[8] Dimroth and Ruck, *Ann.*, 446, 123 (1926); Pfeiffer, Oberlin and Segal, *Ber.*, 60, 111 (1927).

[9] Conant and Fieser, THIS JOURNAL, 46, 1858 (1924).

nificance. It is significant, on the other hand, that the predicted potential for the other tautomer, IIIb, is 0.065 v. higher than the potential found for naphthopurpurin. It is inconceivable that naphthopurpurin has the structure of IIIb and that the discrepancy in the values is due to the inaccuracy of the calculations.

4. Indophenols

An extensive field for the application of the ideas here presented is that of the indophenols, for in the case of any unsymmetrical indophenol two tautomeric forms such as VIa and VIb are possible. Clark and his collaborators, who have carried out a comprehensive study of the electrode potentials of a wide variety of these substances,[10] have recognized throughout the necessity of taking account of the tautomerism of these substances and they have frequently adduced evidence to show that a tautomeric change has taken place during or after the prepaxation of certain of their compounds. On the other hand, they do not appear to have fully appreciated the fact that the tautomers will have different reduction potentials and that the position of the tautomeric equilibrium depends upon the difference between the two values. While it is not now possible with the aid of this principle to interpret much of the data of these authors in terms of the problem of the effect of substituent groups, a few theoretical considerations may serve to clarify the problem. From the facts known about quinones, it may be said that a substituent group always has a greater effect on the potential when it is attached to the quinonoid nucleus than when situated in an adjacent benzene ring, but that the direction of the effect is the same in each instance. If the substituent, X, is an alkyl or an hydroxyl group, both VIa and VIb will be lower in potential than the parent compound, VIa will be lower in potential than the tautomer and will predominate in the equilibrium mixture. Just the reverse is true when the substituent is a halogen or an acidic group and in this case VIb will predominate; but even if more precise predictions were possible, it would be difficult to tell how they correspond with experimental results because the e.m.f. measurements represent equilibrium values. The relationship between such a value and the potential of a single pure tautomer may be defined in the following way. The equation for the electrode potential of one tautomer (α-Oxid), whether alone or in an equilibrium mixture, at such a PH that no dissociation takes place, is



VIa VIb

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[10] (a) Clark and Cohen, *Pub. Health* Repts., 38, 933 (1923); (b) Cohen, Gibbs and Clark, *ibid.*, 39, 381 (1924); (c) *ibid.*, 39, 804 (1924); Gibbs, Cohen and Cannan, *ibid.*, 40, 649 (1925).

$$E^a = E_0^\alpha + 0.059 \log [H^+] + 0.0296 \log [\alpha\text{-Oxid}]/[\text{Red}] \qquad (4)$$

If no tautomer is present, [a-Oxid] is equal to the total concentration of the oxidant $[\text{Oxid}]_T$, and the equation applies in the usual way; otherwise the only determinable concentration, the total concentration of the oxidant, is equal to the sum of [a-Oxid] and [β-Oxid]. Expressing the latter quantity in terms of the former and of the equilibrium constant, K, it is seen that

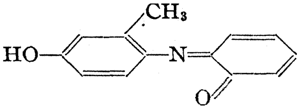
$$[\text{Oxid}]_T = [a\text{-Oxid}] + [\beta\text{-Oxid}]/K$$

whence,

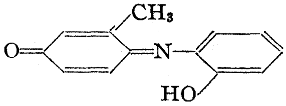
$$E^a = E_0^\alpha + 0.059 \log [H^+] + 0.0296 \log [\text{Oxid}]_T/[\text{Red}] + 0.0296 \log K/(K+1) \qquad (5)$$

If the potential of such a mixture is determined under the usual "normal" conditions ($[H^+ = 1$; $[\text{Oxid}]_T = [\text{Red}]$), the value found, E^a, will differ from the normal potential of the α-oxidant by the amount $0.0296 \log K/(K + 1)$. Thus if two different tautomers had the same potential ($K = 1$), the apparent normal potential of the mixture would be 8.9 mv. lower than the normal potential of either tautomer. This factor obviously complicates the interpretation of data on the effect of simple substitution where the tautomers may be very close to each other in potential.

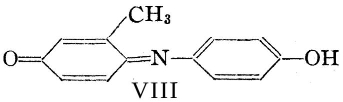
When the two tautomers represent widely different structural types, their potentials may be so far apart that one form will predominate almost exclusively and it should be possible to determine its structure. For example, Cohen, Gibbs and Clark[10c] report measurements with *m*-cresol-o-indophenol, to which, simply on the basis of the mode of preparation, they assign Formula VIIa. There are, however, two reasons for preferring Formula VIIb, the first being that the methyl group will have a greater effect in lowering the potential of the parent compound when it is attached to the quinonoid nucleus than when situated as in VIIa. But a more fundamental difference in the two structures is that one is o-quinonoid, the other p-quinonoid. Not only are o-quinones always much higher in potential than isomeric *p*-quinones by about 0.07 to 0.10 v., but this also applies to the quinonimines,[11] which are closely related to the indophenols in structure. Thus, both because of its *p*-quinonoid structure and because of the location of the methyl group, VIIb most certainly has the lower potential, and the value of this potential would not be expected to differ greatly from that for *m*-cresol-*p*-indophenol, VIII, while the other tautomer



VIIa



VIIb



VIII

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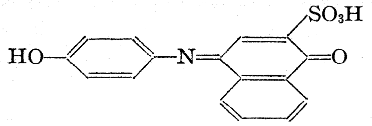
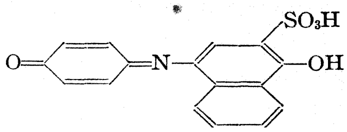
[11] Conant and Pratt, This Journal, 48, 3178 (1926).

must have a potential in the neighborhood of 0.1 v. higher. The experimental results confirm this prediction. The normal potential reported for the "ortho"-indophenol, VII, is 0.647 v.,[10c] while that for the *p*-indophenol, VIII, is 0.632 v.[10b]

Another case to which the same reasoning may be applied is that of 1-naphthol-2-sulfonic acid indophenol,[10a] IX. On considering IXa to be a

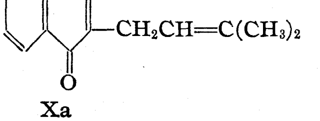

IXa

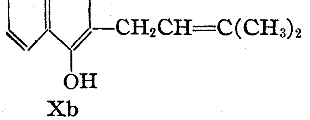

IXb

derivative of phenol-indophenol, for which $E_0 = 0.649$ v.,[10b] adding to this value the known effect of attaching a sulfonic acid group to α-naphthoquinone (0.066 v., av.)[9] and subtracting the difference in the potentials of *p*-benzo- and *p*-naphthoquinonimines (0.175 v.,), a value of 0.540 v. for the potential of IXa is obtained. This, of course, is only a rough estimate, and the same is true of any prediction about IXb. However, it is difficult to see how IXb can differ greatly in potential from phenol-indophenol, $E_0 = 0.649$ v., and this is such a decidedly higher figure that there can be little doubt that the substance corresponds essentially to IXa. The experimentally determined value of 0.544 v., since it agrees well with the above estimate for IXa, clearly demonstrates that this is the case.

5. Lapachol and Related Compounds

There is ample evidence in the foregoing facts not only that the factors governing the tautomeric equilibrium have been correctly defined but also that tautomeric quinones in general exist in solution in a condition of equilibrium. While it seems likely that the latter proposition is an entirely general rule, it is of considerable importance to submit the problem to extensive experimental inquiry. A promising series of compounds for this purpose is that of the type of lapachol, X. With highly substituted quinones of this character, addition to the quinone nucleus is retarded,[2] reduction proceeds slowly (see Experimental Part) and it is conceivable that there might be a condition of delayed equilibrium preventing the less stable tautomer, Xb, from rearranging into Xa. Indeed, according to statements in the literature, one such case is known.


Xa


Xb

For the opportunity to study potentiometrically a number of compounds of the lapachol group, I am greatly indebted to Dr. Samuel C. Hooker, who kindly placed at my disposal pure samples of these materials, some of which had been prepared[12] 34 years ago and had been preserved unchanged. Several similar compounds which have recently been prepared synthetically[13] were included in this study, the results of which are summarized in Table III. In every case the quinone was titrated electrometrically with titanous chloride solution, though two of the determinations with Compound No. 23 were made by titration of the hydroquinone.

Since a number of these substances are very reactive in the sense, for example, that lapachol may be converted by various acidic reagents into α- or β-lapachone or chlorohydrolapachol, some fear was entertained that some such changes might occur on dissolving the compound in the alcoholic hydrochloric acid solution or during the course of the measurements. The results of the measurements themselves lead me to believe that this is not the case. Thus, for example, if hydroxyhydrolapachol suffers any reaction, β-lapachone will surely be among the products formed. This quinone has a potential so much higher than that of the original substance or of any other compound likely to be formed (a-lapachone) that its presence would be unmistakably revealed in the titration curve. However, at the suggestion of Dr. Hooker, whose interest has greatly encouraged me in this work, I attempted to prove that some of these very sensitive compounds remain unaltered. At the completion of a titration, in which, as a rule, 0.05 g. of material was dissolved in 200 cc. of solvent, the solution was exposed to the air until oxidation was complete. Water was then added, the solution was extracted thoroughly with ether, the ethereal solution was washed well with water, dried and the ether evaporated. In many cases the original material was obtained directly in crystalline, and very nearly pure, form; but in every instance it was possible to test the residue with such reagents as ammonia or bisulfite solution for the presence of appreciable quantities of by-products and then to obtain the main product in pure form by crystallization. Compounds No. 13, 18, 19, 20, 22, 28, 31, 32, 36 and 37 were so investigated and in every case the material recovered was found by melting point and mixed melting point determinations to be identical with the original material. Since representatives of all of the types of compound most easily affected are included in this list, it is believed that none of the figures in Table III are in error as a result of any change in the quinones, though they do vary in probable accuracy for reasons discussed in the Experimental Part.

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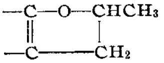
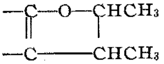
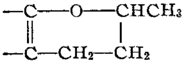
[12] (a) Hooker, J. Chem. *Soc.*, 61, 611 (1892); (b) 69, 1355 (1896); (c) 69, 1381 (1896).

[13] (a) Fieser, THIS JOURNAL, 48, 3201 (1926); (b) 49, 857 (1927).

TABLE III
REDUCTION POTENTIALS AT 25°

Solvent: 50% alcohol, 0.1 N in HCl and 0.2 N in LiCl.

A. Alkyl Hydroxynaphthoquinones

No.	Name	Alkyl group	E_0, v.				ΔE_1, mv.	ΔE_2, mv.	E_0 (Av.), v.
10	2-Allyl-3-hydroxy-1,4-naphthoquinone[13a]	—$CH_2CH{=}CH_2$	0 299	0 298	0 299		18.1	17 7	0.299
11	2-(α-Methylallyl)-3-hydroxy-1,4-naphthoquinone[13b]	—$CH(CH_3)CH{=}CH_2$	.286	288			18 2	15 9	287
12	2-(γ-Methylallyl)-3 hydroxy-1,4-naphthoquinone[13b]	—$CH_2CH{=}CHCH_3$	295	295	.295		18 1	17 9	295
13	Lapachol (X)[12a]	—$CH_2CH{=}C(CH_3)_2$	.285	.289	.286	0 287	17 5	20 0	.287
14	Hydrolapachol[14]	—$CH_2CH_2CH(CH_3)_2$	.286	.285	283		18 6	18 4	.285
15	Chlorohydrolapachol[12a]	—$CH_2CH_2CCl(CH_3)_2$	297	.297			23 7	19 5	.297
16	2-(β-chloropropyl)-3-hydroxy-1,4-naphthoquinone[13a]	—$CH_2CHClCH_3$	305	304			18 0	21 0	304
17	Dibromohydrolapachol[12a]	—$CH_2CHBrCBr(CH_3)_2$	288	294			27	21	291
18	Hydroxyhydrolapachol[12a]	—$CH_2CH_2C(OH)(CH_3)_2$	.290	296	.300	.296	20 8	19 4	295
19	Lomatiol[15,12c]	—$CH{=}CHC(OH)(CH_3)_2$	293	295			23 2	21 5	.294
20	Hydroxy-isolapachol[12b]	—$CH{=}C(OH)CH(CH_3)_2$	3 08	312			2 1 0	1 4 9	.310
21	2-(8-Hydroxypropyl)-3 hydroxy-1,4-naphthoquinone[13a]	—$CH_2CH(OH)CH_3$	.307	309	.307		18 3	17 5	.308
22	*Iso*-β-lapachol[12b]	—$CH{=}CHCH(CH_3)_2$	283	282	.283	281	23 5	20 8	.282
23	2-Benzyl-3-hydroxy-1,4-naphthoquinone[13a]	—$CH_2C_6H_5$	.294	296	.297		19 1	18 9	296
	B 8-Naphthoquinone Derivatives	Heterocyclic Ring							
24	1-Methyl-5,6-benzo-3,4-coumaranquinone[13a,16]		0 406	0 404	0 407		17 4	18 2	.406
25	1,2-Dimethyl-5,6-benzo-3,4-coumaranquinone[13b]		406	.408	.408		1 8 8	1 8 3	.407
26	2-Methyl-7,8-benzo-5,6-chromanequinone[13b]		.399	.398	.400		17 6	18 1	.399

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[14] Monti, *Gazz. chim. ital.*, **45**, II, 51 (1915), prepared this substance by hydrogenating the acetyl derivative, or the hydroquinone triacetate, of lapachol and hydrolyzing and oxidizing the products, but she was unable to effect the hydrogenation of lapachol itself with hydrogen and palladium catalyst. It has been found (experiment of Miss Evalyn W. Brodie) that this hydrogenation is easily accomplished with the aid of the platinum-oxide platinum black catalyst of Roger Adams, the reaction being conducted in alcoholic solution at about 40 lbs. pressure. Oxidation of the hydrolapacholhydroquinone formed takes place on exposing the solution to the air; the product, crystallized from petroleum ether, melted at 88–89' (M. 87–89").

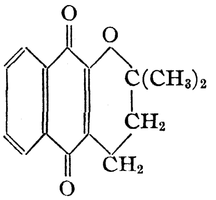
[15] Rennie, *J. Chem. Soc.*, *68, 784* (1895).

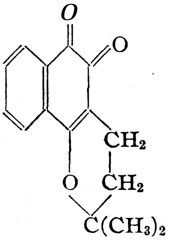
[16] Through an oversight, this compound was incorrectly called 1-methyl-3,4-benzo-5,6-coumaranquinone in the paper in which it is described.

TABLE III (Concluded)

No.	Name	Heterocyclic Ring	E_0, v.				ΔE_1, mv.	ΔE_2, mv.	E_0 (Av.), v.
27	2-Phenyl-7,8-benzo-5,6-chromane-quinone[13a]	—C——O——CHC$_6$H$_5$ ‖ | —C—CH$_2$—CH$_2$	.412	.412	.415	.414	18.7	19.8	.413
28	β-Lapachone (XII)[12a]	—C——O——C(CH$_3$)$_2$ ‖ | —C—CH$_2$—CH$_2$	.403	.403	.402		17.7	18.3	.403
29	Bromo-β-lapa-chone[12a]	—C——O——C(CH$_3$)$_2$ ‖ | —C—CH$_2$—CHBr	.427	.427			18.0	18.0	.427
30	Hydroxy-β-lapa-chone[12a]	—C——O——C(CH$_3$)$_2$ ‖ | —C—CH$_2$—CHOH	.411	.411			18.5	18.0	.411
31	Isopropylfuran-8-naphthoquinone[12b]	—C—O—CCH(CH$_3$)$_2$ ‖ ‖ —C———CH	.460	.460			17.9	17.4	.460
	C. a-Naphthoquinone Derivatives								
32	1-Methyl-4,5-benzo-3,6-coumaran-quinone[13a]	—C—O—CHCH$_3$ ‖ | —C———CH$_2$	.376	.374	.375		18.9	18.2	.375
33	2-Methyl-6,7-benzo-5,8-chromane-quinone[13b]	—C——O——CHCH$_3$ ‖ | —C—CH$_2$—CH$_2$	.307	.307	.308		19.3	18.9	.307
34	a-Lapachone (XI)[12a]	—C——O——C(CH$_3$)$_2$ ‖ | —C—CH$_2$—CH$_2$	.305	.303	.305		18.0	18.3	.304
35	Hydroxy-α-lapa-chone[12b]	—C——O——C(CH$_3$)$_2$ ‖ | —C—CH$_2$—CHOH	.321	.319			20.9	20.3	.320
36	*iso*Propylfuran-α-naphthoquinone[12b]	—C—O—CCH(CH$_3$)$_2$ ‖ ‖ —C———CH	.283	.284			19.9	19.3	.283
	D. Compound of Unknown Structure								
37	Paternò's "Isolapa-chone"	$C_{15}H_{12}O_3$[17,12a]	.366	.365			20.6	23.8	.365

The bearing of these results on the problem of tautomerism may be stated in the following way. In order to determine, in light of the present theory, whether lapachol has the structure of Xa or Xb or is an equilibrium mixture of the two, it is necessary to have some information regarding the relative potentials of the two forms. Of course, judging from the facts known about the simple naphthoquinones, it is probable that the p-quinone form has the lower potential of the two, but this conclusion


XI


XII

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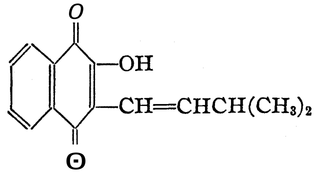
[17] Paternb, *Gazz. chim. ital.*, 19, 622 (1889).

is placed upon a more secure basis by the observation that of the isomers of lapachol, a and β-lapachone (XI and XII), the p-quinone is lower in potential than the isomer by 0.099 v. Lapachol, then, should correspond to Xa. The potential of lapachol has been determined, but there is no altogether sound basis for deciding whether or not the value is consistent with Xa. However, it will be recalled that the potential of hydroxynaphthoquinone is very close to that of a series of its *p*-quinone ethers and, if the *p*-quinonoid structure for the hydroxy compound is granted, it is safe to say that lapachol should correspond with some degree of approximation to a-lapachone, since the latter is similar, in structure and properties, to an alkyl-alkoxy-naphthoquinone. It may be objected that the two substances differ in their degree of saturation and are therefore not comparable, but the figures for lapachol and its hydrogenation product (No. 14) are so close together as to indicate that a double bond situated as it is in lapachol has no appreciable influence upon the potential. At least there is ample justification for stating that lapachol, if it has the structure of Xa, should have a potential closer to that of a-lapachone than to that of β-lapachone. This is in fact the case: the value is 0.017 v. lower than that of a-lapachone and 0.116 v. lower than that of the 8-isomer. Thus both the electrochemical theory and the electrochemical results favor Formula Xa. Hooker[12a] was led to regard lapachol as a *p*-quinone because of its resemblance to hydroxynaphthoquinone, because of its yellow color (a-lapachone is yellow, β-lapachone is red) and because it volatilizes with steam. A further fact which affords strong support of this view is that lapachol reacts only to a very slight extent with sodium bisulfite,[13b] thus differing from almost all o-quinones.

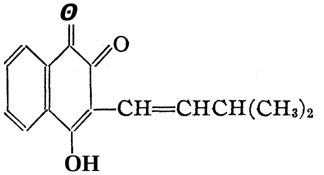
What has been said of lapachol is true of almost all of the hydroxy compounds in the table (Group A). In those cases where the heterocyclic ortho and para quinone isomers are listed under B and C, it is seen that the o-isomer always has the higher potential and that the hydroxy quinone always corresponds much more closely in potential to the p-quinone heterocyclic derivative. This statement is true even though a surprising value appears for one of the heterocyclic compounds, namely, No. **32.** The potential of this p-coumaranquinone is much higher than those of the p-chromanequinones, Nos. **33** and 34, while the isomeric o-coumaranquinone, No. 24, as well as the coumaran, No. 25, are close in potential to the *o*-chromanequinones, Nos. **26** and 28. That No. **32** has the same heterocyclic ring as No. 24 is clearly demonstrated by a series of interconversions described in the Experimental Part; but an interpretation of the potential of the substance is still to be sought.

The potential of *iso*propylfuran-β-naphthoquinone (No. **31)** is higher in relation to the o-coumaran and *o*-chromanequinones than is the isomer, No. **36,** in relation to the corresponding *p*-quinones but, when it is observed that the furan derivatives alone possess unsaturated heterocyclic rings, this is not altogether surprising. A similar situation is found in the relationship between anthraquinone and phenanthrenequinone and with other unsaturated heterocyclic analogs of these compounds.[18]

But even though we are still far from a complete understanding of the relationship between reduction potentials and structure, the peculiarities here noted do not affect the question at issue. The two furan derivatives, Nos. 31 and 36, surely differ very decidedly in potential and the hydroxylic substance, *iso*-β-lapachol (No. 22), agrees closely with the α-isomer in potential and not at all with the @-isomer. Therefore, it is believed that this compound has the structure of XIIIa. This conclusion is supported by the fact that the potential of the compound is just about what would be expected from a consideration of the values for the unsaturated alcohols, Nos. 19 and 20, and from the fact that an alcoholic hydroxyl group produces a slight increase in the potential (compare Nos. 14 and 18), provided that the substance in question is regarded as a *p*-quinone. On the other hand, this conclusion is contrary to the views of Hooker,[12b] who discovered the compound and assigned to it Formula XIIIb. Hooker's reason for adopting the o-quinone formula was largely because the substance is red in color, and to anyone who has had occasion to observe the sharp distinction between the red or orange o-quinones of Group B and the yellow *p*-quinones of Group C, the argument does not lack plausibility. Indeed, in an earlier paper[13b] I made use of this property, in the absence of other evidence, in assigning a tentative structure to the phenyl chromanequinone, No. 27, and the results of the present experiments indicate the correctness of the choice of the o-quinonoid formula in this case, But I do not consider the color of a quinone, even in a group of fairly closely related substances, to be an infallible guide to its structure. There are, in fact, cases in which the rule that *p*-quinones are yellow in color does not hold. Among p-naphthoquinones which are decidedly red in color, mention may be made of naphthazarin, whose structure is not equivocal, and of naphthopurpurin; while a wide variety of halogen substituted 2,5- and 2,6-dialkoxy-*p*-benzoquinones is described in the literature as being red.[19] On the other hand, there is no exception to the



XIIIa



XIIIb

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[18] Fieser and Ames, THIS JOURNAL, 49, 2604 (1927).

[19] (a) Kehrmann, J. *prakt. Chem.*, [2] 40, 365 (1889); (b) Jackson and Bolton, THIS JOURNAL, 36, 1473 (1914); (c) Levine, *ibid.*, 48, 797 (1926); (d) Hunter and

rule that the stable form of a quinone is the form possessing the lowest oxidizing power, unless the present case constitutes an exception and the reduction potential of a quinone, in contrast to the color, is a well defined and well understood physico-chemical constant.

A further fact which supports the contention that *iso*-β-lapachol is a *p*-quinone is that the substance does not react with sodium bisulfite. The bisulfite reaction, like color, is not an absolutely safe criterion of structure, for a few o-quinones, such as Compound No. 27 and 4-phenylmethoxy-1,2-naphthoquinone,[13a] react only to a slight extent with sodium bisulfite; but, considered together with other properties, it is not without value.

The results given in Table III permit of several interesting observations concerning the relationship between reduction potential and structure, the more important of which will be briefly mentioned. While an hydroxyl group attached to a quinonoid nucleus lowers the potential by about 120 mv.,[9] an hydroxyl group in a saturated or unsaturated side chain or in a saturated heterocyclic ring raises the potential by from 8 mv. to 28 mv., the effect being greater the closer the group is to the quinonoid ring. The quinonoid substitution of chlorine or bromine causes an average increase in potential of 18 mv.,[9] and side chain substitution of these elements produces about the same effect. An increase in the size of an alkyl group, or an increase in the number and character of the alkyl or aryl groups attached to a saturated heterocyclic ring, produces no appreciable alteration in the potential. The presence of a double bond in a side chain has little influence on the potential, regardless of its position.

6. Certain Alkoxy Naphthoquinones

Reference has been made to the fact that hydroxynaphthoquinone and its *p*-quinone ethers have about the same reduction potentials and that this fact, granting the assumption of the *p*-quinonoid structure of the hydroxy compound, indicates that the hydroxyl and alkoxyl groups have approximately the same potential-lowering effect. In an attempt to establish the correctness of this conclusion by independent evidence and thus further establish the correctness of the reasoning of Section 2, several 2-methoxy-3-alkyl-1,4-naphthoquinones, such as the methyl ether of lapachol, were prepared and examined potentiometrically, the idea being that, since lapachol exhibits little tendency to exist in an o-quinonoid form,[20] a comparison of it with its ether is of somewhat greater significance than

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Levine, *ibid.*, 48, 1608 (1926). It is of significance that certain diaryl-*p*-benzoquinones [(e) Pummerer and Prell, Ber.. 55, 3111 (1922); (f) Pummerer and Fiedler, *Ber.*, 60, 1439 (1927)], as well as 2,5-dihydroxy-*p*-benzoquinone [(g) Scholl and Dahll, *Ber.*, 57, 81 (1924)], have been obtained in both a yellow form and an orange or red form.

[20] The failure of lapachol to react readily with sodium bisulfite is evidence of this point.

in the case of hydroxynaphthoquinone. But no satisfactory potential measurements could be obtained with any of these compounds, the difficulty apparently being that equilibrium between the quinone and its reduction product was never attained, or was reached extremely slowly.

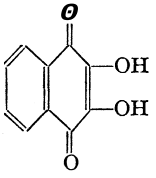
Isonaphthazarin and its mono- and dimethyl ethers were next examined (see Table IV), but the results are inconclusive. A consideration of the reduction potentials of a-naphthoquinone (E_0 = 0.483 v.) and of hydroxynaphthoquinone (E_0 = 0.356 v.) shows that one quinonoid hydroxyl group produces a potential lowering of 0.127 v. If isonaphthazarin is regarded as a p-quinone (XIV), it appears that a second hydroxyl group has an effect of only 0.074 v., or that the effect of each of the two groups is only 0.100 v. While such a result is not without parallel,[9] it is equally permissible to consider isonaphthazarin to be a β-naphthoquinone derivative, when the effect of each of the two hydroxyl groups is represented by a quantity, 0.147 v., which is somewhat more comparable with the value for one such group.

TABLE IV

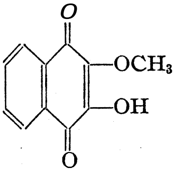
REDUCTION POTENTIALS AT 25°[21]

Solvent: 50% alcohol, 0.1 *N* in HCl and 0.2 N in LiCl.

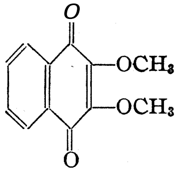
No.		E_0, v.				ΔE_1, mv.	ΔE_2, mv.	E_0 (av.)
38	Isonaphthazarin	0.282	0.281	0.282	0.282	17.9	18.1	0.282
39	Isonaphthazarin monomethyl ether	.330	.328	.329	.330	18.7	19.7	.329
40	Isonaphthazarin dimethyl ether	.385	.387	.388		20.2	18.9	.387



XIV



XV



XVI

The red color of isonaphthazarin is hardly indicative of an o-quinonoid structure in view of the fact that naphthazarin is likewise red. Negative evidence in favor of the p-quinone formula is furnished by the fact that sodium bisulfite is without action on the substance, while the conversion of the compound into XVI (yellow, insoluble in bisulfite solution) by the action of diazomethane affords some support of this view. However, the evidence is not sufficiently conclusive to warrant a final decision, and consequently the relationship of isonaphthazarin to its ethers, XV and XVI, which are probably *p*-quinones, cannot be adequately defined, though the fairly regular increase in potential from XIV to XV to XVI is suggestive. I am inclined to consider that isonaphthazarin is a p-quinone, that in the dihydroxy series an ether has a considerably higher potential than

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[21] Determined by titration of the hydroquinones with benzoquinone solution

the corresponding hydroxy compound, that in the series of the alkylhydroxy-naphthoquinones an ether is only slightly higher in potential than the hydroxy compound (compare a-lapachone and hydrolapachol), and that there is no difference between the two in the case of hydroxynaphthoquinone. But these conclusions, even if they were adequately established, would not serve to answer the question stated at the beginning of this section.

7. The Influence of the Hydrogen-Ion Concentration on the Position of the Tautomeric Equilibrium

The equations given above apply only to solutions which are of such acidity or of such a character that no ionization of either the oxidant or the reductant takes place. In view of the striking color changes which frequently accompany the dissolution of hydroxy quinones in alkali, and particularly because it has often been assumed that such a color change is the result of a process of tautomerization, it is of considerable interest to extend the simple equations to include solutions of any hydrogen-ion concentration.

The case of a quinone containing a single dissociable hydroxyl group, whose hydroquinone has three hydroxyl groups, will be considered (e. g., hydroxynaphthoquinone). A general expression for the electrode potential of a solution of one pure tautomer (a-Oxid) of any acidity is as follows[22]

$$E^{\alpha} = E_0^{\alpha} + 0.0296 \log [\alpha\text{-Oxid}]_T + \underbrace{0.0296 \log (k_1k_2k_3 + k_1k_2[\mathrm{H}^+] + k_1[\mathrm{H}^+]^2 + [\mathrm{H}^+]^3)/[\mathrm{Red}]_T}_{\textbf{Term } (a)} - 0.0296 \log (k_{\alpha} + [\mathrm{H}^+]) \qquad (6)$$

in which $[\alpha\text{-Oxid}]_T$ and $[\mathrm{Red}]_T$ are the total concentrations of the oxidant and reductant and thus account for both the dissociated and undissociated material, k_1, k_2 and k_3 are the three dissociation constants of the reductant, and k, is the dissociation constant of the quinone, or oxidant. This equation applies equally well to the potential of the tautomer in an equilibrium mixture, provided that a means can be found for evaluating $[\alpha\text{-Oxid}]_T$. A similar equation applies to the second tautomer (β-Oxid) and, since the two tautomers have a common reduction product, Term (a) is identical in each case and we may write

$$E^{\beta} = E_0^{\beta} + 0.0296 \log [\beta\text{-Oxid}]_T + \textbf{Term } (a) - 0.0296 \log (k_{\beta} + [\mathrm{H}^+]) \qquad (7)$$

It is obvious that in an equilibrium mixture the potentials of the two systems must be identical ($E^{\alpha} = E^{\beta}$). On equating (6) and (7) the following expression results:

$$0.0296 \log [\alpha\text{-Oxid}]_T/[\beta\text{-Oxid}]_T = (E_0^{\beta} - E_0^{\alpha}) + 0.0296 \log (k_{\alpha} + [\mathrm{H}^+])/(k_{\beta} + [\mathrm{H}^+]) \qquad (8)$$

Defining a general tautomeric equilibrium constant, or the ratio of the

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[22] *Compare Clark and Cohen, Pub. Health Repts.*, **38,** 666 (1923).

concentrations of the two reactants in any solution, thus: $K' = [\alpha\text{-Oxid}]_T/[\beta\text{-Oxid}]_T$, Equation 8 becomes

$$\log K' = (E_0^\beta - E_0^\alpha)/0.0296 + \log (k_\alpha + [H^+])/(k_\beta + [H^+]) \qquad (9)$$

Equation 9 shows that in acid solutions where $[H^+]$ is considerably greater than k_α or k_β, the equilibrium constant is a function only of the difference in the normal potentials of the tautomers, that is, the equation reduces to Equation 4, which was derived in a different way. In alkaline solutions where $[H^+]$ is inappreciable with respect to k_α and k_β, the equilibrium constant is again independent of $[H^+]$ but its logarithm differs from that of the value in acid solution by the term $\log (k_\alpha/k_\beta)$. These relationships for the extremes of acidity and alkalinity where the quinones exist as undissociated molecules or as ions, respectively, may be expressed as follows

$$\log K(\text{un-ionized}) = (E_0^\beta - E_0^\alpha)/0.0296 \qquad (10)$$

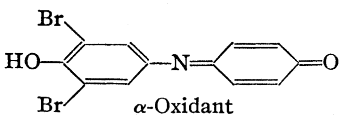
$$\log K(\text{ionized}) = (E_0^\beta - E_0^\alpha)/0.0296 + \log (k_\alpha/k_\beta) \qquad (11)$$

On combining these expressions

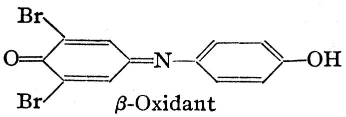
$$K\ (\text{ionized}) = K\ (\text{un-ionized})\ (k_\alpha/k_\beta) \qquad (12)$$

The extent of the change in the equilibrium constant on passing from an acid to an alkaline solution is thus dependent upon the ratio of the dissociation constants of the two tautomers. If these constants are the same, as is probably approximately true in the case of hydroxynaphthoquinone, no change in the equilibrium constant will result.

The above equations apply equally well to the indophenols. In a number of the substances of this type which were examined by Clark and his collaborators,[10] the hydroxyl group of one tautomer is surrounded by halogen atoms and will consequently have a dissociation constant greater than that of the second tautomer in which this group is situated in a benzene ring. As a result, the composition of the equilibrium mixture will vary with the PH of the solution in a manner defined by Equation 9. Clark, observing that the apparent dissociation constant of 2,6-dibromophenol-indophenol is considerably greater than the dissociation constant of phenol-indophenol, concluded, with reason, that the predominant tautomer was that in which the hydroxyl group is in the halogen substituted ring[10b,c] (XVIIa) but it must be noted that such statements apply only in the PH range at and beyond which dissociation of the oxidant becomes appreciable. It is reasonable to suppose that the ratio of the dissociation constants of the two tautomeric forms of XVII is approximately



α-Oxidant
XVIIa

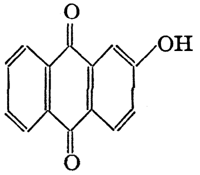


β-Oxidant
XVIIb

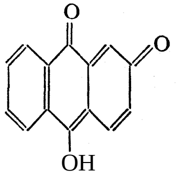
equal to the ratio of the apparent dissociation constant of this substance to the dissociation constant of phenol-indophenol, whence: $k_\alpha/k_\beta = 250$. Then, by Equation 12, the tautomeric equilibrium constant of the ionized quinones is two hundred and fifty times as great as that of the quinones in the un-ionized condition. The process of dissociation greatly increases the proportion of the a-oxidant in the equilibrium mixture. Obviously the fact that this tautomer predominates when the quinones are dissociated furnishes no basis for considering that this is true under any other conditions.

The case of naphthopurpurin, III, is also illustrative. The fact that this substance, like hydroxynaphthoquinone, is a stronger acid than naphthoquinones with hydroxyl groups only in the benzenoid nucleus (see Experimental Part) might be taken as evidence that the one hydroxyl group of doubtful position is attached to the quinone nucleus as in IIIa, which may be termed the a-form. But the argument only applies to the ionized substance. The product of the three dissociation constants of this a-form will surely be greater than the corresponding product for the β-form, IIIb, which means that K(ionized) is greater than K(un-ionized), and again ionization favors the a-form.

Finally, it is of interest to consider the possibility of tautomeric change in the hydroxyanthraquinone series. The properties of the β-derivative, XVIII, for example, leave little doubt that under all ordinary conditions the substance corresponds to XVIIIa (a-form), and yet, largely in order to account for certain color phenomena, the assumption has often been made that a rearrangement to XVIIIb (β-form) takes place on the formation of salts of this substance.[23] Now the normal reduction potential of XVIIIb, which has an extended quinonoid structure similar to that of amphi-naphthoquinone, would surely be much the higher of the two; consequently the constant for the un-ionized quinones must be a large number, indicating that XVIIIa predominates. A change to XVIIIb on ionization can only take place if the dissociation constant of this substance is considerably less than that of XVIIIa. But from what is known regarding the acidic strength of hydroxy quinones, it appears highly probable that the



XVIIIa



XVIIIb

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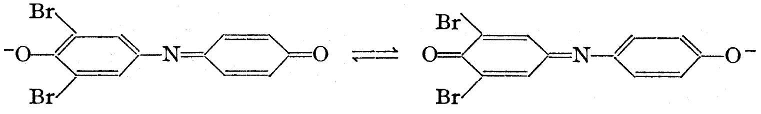
[23] Scholl and Zincke, Ber., 51, 1419 (1918); this paper contains references to the earlier literature; Barnett, "Anthracene and Anthraquinone," D. Van Nostrand Co., New York, 1921, p. 252; Goodall and Perkin, *J. Chem. Soc.*, 125, 470 (1924); Moir, *ibid.*, 1927, 1809.

dissociation constant of XVIIIb is not less, but greater, than that of the more stable tautomer, and this reasoning leads to the conclusion that under no conditions can a tautomeric change in the manner indicated occur.

Before concluding this discussion it seems advisable to call attention to the question of the validity of postulating the existence of a tautomeric equilibrium between ions. While it is hardly appropriate to consider in any detail the subject of the mechanism of reactions in connection with a problem which is concerned solely with equilibria, some statement of the possibilities in this direction is necessary. A conception which has been of service in developing the present theory is that each tautomer preserves its structure on ionization but that a rearrangement of its linkages and a shift of the charge from one center to another is possible. Thus the ions of XVIIa and XVIIb would have the following structures and they would be in equilibrium with each other


IXa IXb

An alternate view is that the change from one ion to the other takes place only by the combination of the ion with a hydrogen ion, tautomeric change, and dissociation. The resultant equilibrium would be the same in either event.

On the other hand, one may question the existence of tautomers in the ionic state and prefer to consider that the dissociation of the two tautomers produces a single ion, an ion to which it is impossible to assign a formula such as IXa or IXb. It then would be necessary to suppose that one oxygen atom of this ion has a different tendency than the other oxygen to combine with a hydrogen ion, for the two un-ionized molecules have, or can have, different dissociation constants. Thus the conception of a single ion with two tendencies to combine with hydrogen ion is contrasted with the view that there are two ions, each of which has a definite affinity for hydrogen ion. If the former view were adopted it would be necessary to consider the whole question of tautomerism from a point of view different from that given above and with the use of a new terminology. In this paper preference has been given to the latter idea, which permits the use of ordinary organic formulas and which introduces no novel conceptions, but I do not wish to indicate that this view is considered to be the only one by means of which it is possible to arrive at the conclusions here presented.

I expect to consider the problem of the tautomerism of the amino quinones in a future communication.

Experimental Bart

Alkoxy-naphthoquinones.—The quinones listed in Table I have been described previously,[2] with the exception of the two *n*-propoxy derivatives. The latter substances were prepared in the usual manner by the action of n-propyl iodide on the silver salt of hydroxynaphthoquinone in benzene suspension, 10% of the salt being converted into hydroxynaphthoquinone, while of the remainder 74% was converted into the o-quinone ether and 13% into the p-quinone ether. The p-quinone ether was also prepared by esterification of the hydroxy compound with n-propyl alcohol and hydrogen chloride.

4-(*n*-Propoxy)-1,2-naphthoquinone crystallizes from ligroin-benzene in the form of very long, thick, orange-yellow needles, m. p. 116°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.97; H, 5.66.

2-(*n*-Propoxy)-1,4-naphthoquinone crystallizes from ligroin or from water, forming long, pale yellow needles melting at 91°.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 72.17; H, 5.74.

The remarkable ease with which hydrolysis of the o-quinone ethers of this series takes place has been noted.[2] On examining samples which had been prepared one year previously and stored in cork-stoppered specimen tubes, it was observed that specimens of the ethyl and allyl[13a] ethers had lost their luster; they were yellow and not orange-yellow; they were partially soluble in cold ammonia solution and a marked odor of allyl alcohol was apparent in the tube containing the allyl derivative. Analysis of the latter (dried) material, which was originally an analyzed sample of alloxy-β-naphthoquinone, indicated that it was a mixture of 46.5% of the ether and 53.5% of hydroxynaphthoquinone (calcd.: C, 70.34; H, 4.03. Found: C, 70.34; H, 4.04).

Alkyl Methoxynaphthoquinones.—Since compounds of the type of lapacbol are strongly acidic substances, it was to be expected that diazomethane would attack the hydroxyl group before adding to the double bond. This was the case, for compounds were obtained which, from the results of analysis and of hydrolysis experiments, were found to be ethers; their melting points and analyses are listed in the accompanying table.

TABLE V

2-ALKYL-3-METHOXY-1,4-NAPHTHOQUINONES

Alkyl group	M. p., °C.	Calcd., % *C*	Calcd., % H	Found, % *C*	Found, % H
—$CH_2CH{=}C(CH_3)_2$	53	74.97	6.30	74.99	6.28
—$CH_2CH{=}CHC_6H_5$	90.5	78.92	5.30	78.92	5.36
—$CH_2C_6H_5$	83.5	77.67	5.07	77.56	5.10
—$CH(C_6H_5)_2$	112.5	81.33	5.12	81.26	5.12

In each case the compound was obtained, on evaporating the ethereal solution, in the form of an oil which solidified on rubbing. Crystallized from ligroin or petroleum ether, the substances, with exception of the last one, formed short, well-formed, yellow needles. The diphenylmethyl derivative formed hard lumps of crystal aggregates. The substances are all very readily soluble in the usual organic solvents and very sparingly soluble in water. Unlike the alkoxy-α-naphthoquinones, they are hydrolyzed with considerable difficulty by sodium hydroxide or alcoholic alkali. Triphenylmethplhydroxynaphthoquinone did not react with diazomethane under conditions suitable for the preparation of the above compounds.

Polyhydroxynaphthoquinones.—The most convenient method of preparing naphthazarin is that patented by Baeyer and Co.[24] and more fully described by Charrier and

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[24] Ger. Pat. 71,386.

Tocco.[25] Fuming sulfuric acid of the concentration called for not being available, it was found that satisfactory results were obtained by adding a solution of 25 g. of sulfur in 375 cc. of 18% fuming sulfuric acid to a well-stirred suspension of 50 g. of 1,5-dinitronaphthalene in 230 cc. of concd. sulfuric acid. The temperature was not allowed to rise above 60°, though it is sometimes necessary to maintain this temperature by external heating for a short time in order to complete the reaction. The product was worked up in the usual way; average yield, 26 g. A sample for the potential measurements was pursed by sublimation.

The preparation of naphthopurpurin at first presented some difficulties because neither this substance nor naphthazarin is easily identified. Alkaline solutions of mixtures of the two quinones can be prepared which are indistinguishable in color from an alkaline solution of naphthopurpurin. Finally, recourse was had to potentiometric analysis. Since the two quinones differ decidedly in reduction potential (Table II) a titration curve (of the catalytically prepared hydroquinone solution) serves to reveal the presence of one of these substances in a mixture consisting largely of the other, and it furnishes a fairly accurate idea of the relative concentrations. The titration curve consists of two distinct logarithmic curves and it is easily interpreted. Only traces of naphthopurpurin were detected in samples prepared according to Jaubert[26] by grinding together 4 g. of naphthazarin, 8 g. of finely powdered manganese dioxide and 8 cc. of concd. sulfuric acid. On dissolving the same quantity of the quinone in 30 cc. of concd. sulfuric acid, slowly sprinkling in 8 g. of manganese dioxide, with very vigorous stirring, and heating the mixture for twenty minutes at 125°, a product containing equal parts of naphthazarin and naphthopurpurin resulted. At 160° the material was largely destroyed.

The manganese dioxide method was soon abandoned for a modification of a method described in the patent literature,[27] in which the oxidation of naphthazarin is accomplished by the action of air in an alkaline'solution. In order to separate the product from traces of unchanged material, advantage was taken of the fact that naphthopurpurin is much the stronger acid of the two It is also of advantage to purify the monosodium salt, for naphthopurpurin itself does not crystallize at all well from any of the available solvents.

A solution of 5 g. of naphthazarin in 1.2 liters of water containing 35 cc. of 6 N sodium hydroxide solution was heated on the water-bath, with a rather rapid stream of air passing through the solution, for four and one-half hours. The solution was rendered just acid with acetic acid, when the color changed from fuchsin-red to a dull red, cooled and a slight amount of precipitated material was removed by filtration. In order to obtain the sodium salt, the solution is best concentrated to a volume of about 500 cc. and treated with an equal volume of saturated sodium chloride solution. The dark red salt then separates in the form of a fine powder. It dissolves rather readily in water but does not crystallize without the use of sodium chloride and it was not obtained in a form entirely free from this reagent. The barium salt, obtained by adding barium chloride solution to a hot solution of the sodium salt, is only moderately soluble in water and it can thus be washed free of inorganic material.

Anal. Calcd. for $(C_{10}H_5O_5)_2Ba$: Ba, 25.08. Found: 24.90.

Naphthopurpurin prepared from the reprecipitated sodium salt corresponded in properties with Jaubert's material. In its strongly acidic character, this quinone closely

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[25] Charrier and Tocco, *Gazz. chim. ital.*, **53**, 431 (1923). This paper is incorrectly quoted in *Chemical Abstracts,* 18,254 (1924).

[26] Jaubert, *Compt. rend.*, 129, *684* (1899).

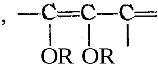
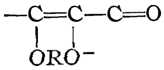
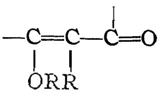
[27] Ger. pat. 167,641.

resembles 2-hydroxy- and 2,6-dihydroxy-1,4-naphthoquinone. All of these substances dissolve readily in sodium acetate solution and are precipitated from an alkaline solution only by a large excess of acetic acid. This property is not shared by naphthoquinones containing hydroxyl groups only in the benzenoid ring, such as juglone or naphthazarin, while the presence of a second hydroxyl group or of an alkyl group in the quinonoid nucleus somewhat decreases the acidic strength of hydroxynaphthoquinone.

2,6-Dihydroxy-1,4-naphthoquinone was obtained from 6-hydroxy-1,2-naphthoquinone[28] in the manner described by Dimroth and Kerkovius.[29] Some improvement was effected in the preparation of the starting material, 2.6-dihydroxynaphthafene. Schaeffer's salt (150 g.) was fused with potassium hydroxide according to the directions of Willstätter and Parnas[30] but, since it appears that 2,6-dihydroxynaphthalene readily undergoes decomposition in alkaline solution, the product was not cooled and dissolved in water, but the melt, while still hot, was ladled out into a mixture of 700 cc. of concd. hydrochloric acid and enough ice to give a final volume of about 5 liters. The crude product was crystallized with the use of animal charcoal from 2 liters of water, when it was observed that some decomposition occurs during the process of dissolution unless the suspension is vigorously stirred. The yield of light brown material melting at 209° (uncorr.) was 50 g., and the substance dissolved in alkali with the color and the fluorescence of the product obtained by the above-named authors after a lengthy process of purification.

Isonaphthazarin-dimethyl Ether.—Isonaphthazarin[31] was crystallized from glacial acetic acid and the sample melted at 282°. On adding 1.1 g. of this substance to an ethereal solution of diazomethane prepared from 5 cc. of nitrosomethylurethan, a rapid evolution of nitrogen took place, the red crystals soon dissolved and long, yellow needles were deposited. Recrystallized from ether, the substance melted at 115°. It is readily soluble in alcohol or ligroin, very readily soluble in ether or benzene and insoluble in water or in bisulfite solution.

Anal. Calcd. for $C_{12}H_{10}O_4$: C, 66.04; H, 4.62. Found: C, 65.86; H, 4.65.

Isonaphthazarin Monomethyl Ether.—The action of alkali on the above substance is very interesting because a single ether group is attacked and the resulting substance is resistant to hydrolysis to a marked degree. In this behavior, 2,3-dimethoxy-1,4-naphthoquinone closely resembles 2,3-dichloro-1,4-naphthoquinone, only one of whose chlorine atoms is replaced by the action of alkali or of amines. The latter reactions have been enumerated and discussed by Fries and Ochwat,[32] who regard the substitution reactions as involving either a "mobile" atom or 1,4-addition. While I am inclined to consider the hypothesis of 1,4-addition as the more attractive, particularly as applied to the hydrolysis of alkoxy naphthoquinones,[2] it seems odd that the 1,4-addition of alkali to the system,  $-\underset{|\atop \mathrm{OR}}{\mathrm{C}}=\underset{|\atop \mathrm{OR}}{\mathrm{C}}-\underset{|}{\mathrm{C}}=\mathrm{O}$, takes place readily, while a similar addition to the systems  $-\underset{|\atop \mathrm{OR}}{\mathrm{C}}=\underset{|\atop \mathrm{O^-}}{\mathrm{C}}-\mathrm{C}=\mathrm{O}$ and  $-\underset{|\atop \mathrm{OR}}{\mathrm{C}}=\underset{|\atop \mathrm{R}}{\mathrm{C}}-\overset{|}{\mathrm{C}}=\mathrm{O}$ (lapachol methyl ether) occurs only very slowly.

The dimethyl ether was warmed on the water-bath for a short time with 1% sodium hydroxide solution. It soon dissolved with the production of a deep red solution from

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[28] Kehrmann, *Ber.*, **40**, 1962 (1907).

[29] Dimroth and Kerkovius, *Ann.*, **399**, 36 (1913).

[30] Willstätter and Parnas, *Ber.*, **40**, 1410 (1907).

[31] Zincke and Ossenbeck, *Ann.*, **307**, 11 (1899).

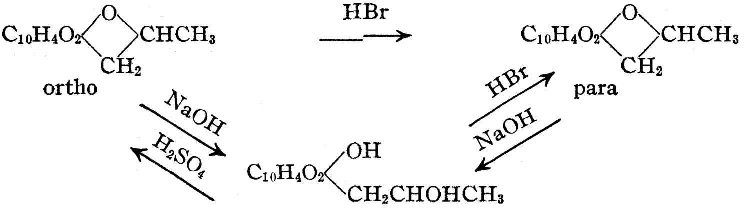
[32] Fries and Ochwat, *Ber.*, 56, 1291 (1923).

which, on acidification, a yellow product separated in quantitative yield. The compound crystallized from water, in which it dissolves readily at the boiling point, in the form of fluffy clusters of small needles; from ligroin-benzene solution stout yellow needles were deposited, m. p. 152°. Like hydroxynaphthoquinone, the substance forms a soluble bisulfite addition product. Prolonged boiling of the alkaline solution of the ether failed to bring about further hydrolysis.

Anal. Calcd. for $C_{11}H_8O_4$: C, 64.70; H, 3.95. Found: C, 64.43; H, 4.14.

1-Methyl-4,5-benzo-3,6-coumaranquinone (No. 32).—The peculiar position of the potential of this compound suggested the possibility that the structure ascribed to it[13a] might be incorrect. The compound had been previously obtained only as a by-product in the conversion of 2-allyl-3-hydroxy-1,4-naphthoquinone into its hydrochloride and, in very small yield, directly from the latter substance, and it had not been adequately studied. It has now been found that a better yield can be obtained as follows. Two g. of allyl-hydroxy-naphthoquinone was dissolved in 20 cc. of glacial acetic acid, 10 cc. of constant-boiling hydrobromic acid was added and the solution was heated on the water-bath for one and one-fourth hours. On pouring the solution into a large volume of water, a brown oil separated and soon solidified. The collected material was treated with ammonia solution until the extract was no longer red and it was then dissolved in glacial acetic acid, a small quantity of chromic acid was added to destroy oily impurities, the solution was diluted and allowed to cool. A further crystallization from ligroin gave a pure product, m. p. 166–167°; yield, 0.5 g.

On boiling this substance with diluted sodium hydroxide solution, a deep red solution results and on acidification there is precipitated a compound which has the appearance of 2-(β-hydroxypropyl)-3-hydroxy-1,4-naphthoquinone. The latter substance was previously obtained from the isomeric o-coumaranquinone and the relationship of the two isomers to each other would be adequately established by proving the identity of the two samples of the alcohol. Such a comparison, however, was not convincing because the melting point of the material depends to some extent upon the rate of heating, the state of subdivision and probably upon the condition of the glass surface of the capillary. On the other hand, each specimen was converted into the *p*-coumaranquinone (No. 32), a substance easily identified, by following the above directions for the allyl derivative. The o-coumaranquinone, No. 24, was likewise transformed into its isomer by a similar treatment, and it could be obtained from the hydroxypropyl derivative by the action of concd. sulfuric acid. This series of conversions, summarized as follows



proves that the heterocyclic ring is the same in the two isomers.

E.m.f. Measurements.—The procedure for carrying out a titration with a hydroquinone solution was as follows. Sufficient of the quinone for two determinations was dissolved in a suitable solvent and the solution was placed, together with some 5% platinized asbestos, in a 500cc. bottle. The rubber stopper of this bottle carried tubes for the admission and outlet of hydrogen and a tube extending to the bottom and ending in a wide, flared tube fitted with a filter plate covered with filter paper and secured in position with gauze and thread. To the upper end of this tube was attached a short section of pressure tubing into which a glass tube could later be fitted for the purpose of removing the hydroquinone solution. This filter tube was freed of solution and of air with a stream of hydrogen and then closed. The air in the bottle was displaced by hydrogen, the bottle was closed to the atmosphere and the whole was shaken mechanically, the bottle being connected to a hydrogen reservoir under a slight pressure At the same time the oxidation-reduction half-cell vessel was freed of oxygen with a stream of nitrogen and, when reduction of the quinone was complete, connection between this vessel and the bottle was made through a nitrogen-filled tube and half of the solution was transferred under hydrogen pressure. The solution was then swept with nitrogen while acquiring the temperature of the thermostat and a titration with a solution of a suitable oxidizing agent was carried out. The remainder of the solution in the bottle was shaken for an additional period of time before the second titration; consequently, if reduction were incomplete in the first instance, this fact would be revealed by a lack of agreement in the two determinations. While the shape of the titration curve usually affords sufficient evidence of incomplete reduction or of air leakage, it is of value to have this additional check on the method, particularly because in a few instances the quinone solution does not lose its color on hydrogenation. This was generally true in the case of certain anthraquinones to be described in a future paper. In some instances hydrogenation was so slow in the presence of platinized asbestos that the platinum-oxide platinum black catalyst of Adams[33] was employed.

The alcoholic phosphate buffer solution mentioned in Table I was prepared by diluting **1.9** liters of **a** solution 0.087 M in potassium dihydrogen phosphate and 0.087 M in disodium hydrogen phosphate to a volume of 3.5 liters with **95%** alcohol. It was estimated that the resulting solution contains approximately 37% of alcohol.

Reference has been made to the failure to obtain satisfactory measurements with any of the compounds listed in Table V. To this list may be added 2-cinnamyl-, 2-diphenylmethyl- and 2-triphenylmethyl-3-hydroxy-1,4-naphthoquinone. With all of these compounds the potentials were not constant, the end-point was uncertain and the approximately determined normal potentials differed in duplicate titrations by as much as 20 mv. It will be noted that all of these substances are *p*-quinones completely substituted with large groups.

In the lapachol series (Table III) considerable difference in the behavior of the various compounds was noted. Since the determinations were all carried out in very nearly the same manner, the time required for the actual titration is of some significance in indicating, it is believed, the relative velocities of reduction. With the hydroxy-*p*-quinones of Group A, from one and one-half to three hours was required; with the heterocyclic *p*-quinones (Group C), the titrations occupied from one to two hours, while with the heterocyclic o-quinones (Group B), a titration was completed in about twenty minutes, even in the case of the phenylated derivative, No. 27. In Groups A and C, reduction was the slowest with the most highly substituted compounds such as dibromohydrolapachol and hydroxy-a-lapachone. These facts may be interpreted in the following manner. Regardless of their character, substituents attached to an *o*-naphthaquinone cannot hinder the 1,4-addition of hydrogen because

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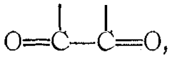
[33] Voorhees with Adams, THIS JOURNAL, 44, **1397 (1922).**

they are not directly connected to the 1,4-system:  $O=\overset{|}{C}-\overset{|}{C}=O$, and because they are joined to a double bond which retains the same position in the hydroquinone. In a *p*-naphthoquinone, on the other hand, the substituents are attached to the 1,6-conjugated system to the ends of which hydrogen adds.[34] The substituents, to a degree depending upon their size and character, retard the velocity of the addition of hydrogen because the 1,6-system suffers rearrangement as a result of the process of reduction and the double bond between the substituted carbon atoms becomes a single bond. Ring formation between the substituent groups decreases somewhat the hindrance of these groups.

In conclusion, I wish to express my thanks to Dr. Samuel C. Hooker for generously supplying me with a number of compounds for this investigation, and to acknowledge my indebtedness to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for a grant which has aided this work.

Summary

The constant of the equilibrium between the tautomers, hydroxy-α-naphthoquinone and hydroxy β-naphthoquinone, depends upon the reduction potentials of these two forms, according to the equation

$$\log K = (E_0^{\beta} - E_0^{\alpha})/0.0296$$

where $K = [\alpha\text{-Form}]/[\beta\text{-Form}]$. In order to estimate the value of K, the reduction potentials of a number of ethers of the α and β forms have been determined, with the result that, as an approximation, $K = 502$.

In order to test the principle that that tautomer will predominate which has the lower reduction potential, the potentials of the two tautomeric forms of naphthopurpurin have been estimated from the values for certain related compounds, and it has been found that the actual potential of naphthopurpurin corresponds closely with the value estimated for the tautomer of lower potential. Similar analysis of the results of Clark for two indophenols furnishes additional support of the point at issue.

The reduction potentials of a number of compounds of the type represented by lapachol are consistent with this principle and, with one exception, the electrochemical results are consistent with all other known properties of these substances. It is considered that, contrary to the views of the discoverer of the compound, *iso*-β-lapachol is a *p*-quinone.

The variation of the tautomeric equilibrium constant with the hydrogen-ion concentration has been formulated, and it has been shown that the

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[34] Kohler and Butler, THIS JOURNAL, 48, 1036 (1926). The 1,6-addition to *p*-quinones of the magnesium subiodide of Gomberg and Bachmann, *ibid.*, 49, 236 (1927), as well as the 1,4-addition of this reagent to *o*-quinones, has been established by boiling the dark green suspension which results with acetyl chloride, when the hydroquinone diacetate is formed in good yield.

ratio of the equilibrium constant of the undissociated tautomers to the constant for the completely ionized substances is equal to the ratio of the dissociation constants of the two hydroxy quinones.

BRYN MAWR, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

2-HYDROXY-1,4-ANTHRAQUINONE

BY LOUIS F. FIESER

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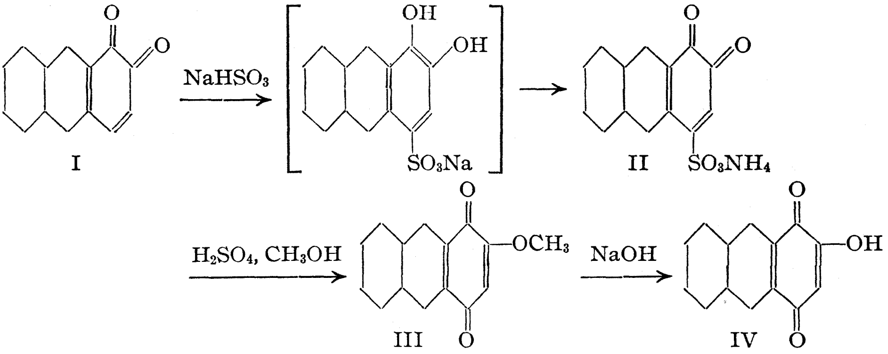
The interest attaching to the properties of hydroxynaphthoquinone, in particular with regard to the abnormal course of its alkylation reactions[1] and the position of the equilibrium between its tautomeric forms,[2] renders it a matter of some importance to examine the hitherto unknown compound named in the title. The chemistry of anthracene is so different from that of naphthalene that it should be possible to determine, in this way, if the phenomena referred to are at all general.

The most satisfactory method found for the preparation of 2-hydroxy-1,4-anthraquinone is indicated as follows



The conversion of II into III involves hydrolysis of the sulfonate group, tautomeric change to IV, and esterification. Good yields were obtained in all of the reactions when pure materials were employed, but it was found most convenient to use crude 1,2-anthraquinone,[3] when the over-all yield from β-anthrol was only 23% of the theoretical. The sulfonate, II, was also obtained from 1-nitroso-2-anthrol.[3] This was converted, by acidifying its solution in sodium bisulfite solution, into 1-amino-2-anthrol-4-sulfonic acid, and the latter was easily oxidized to the quinone, II, by nitric acid. The yield, however, was very poor.

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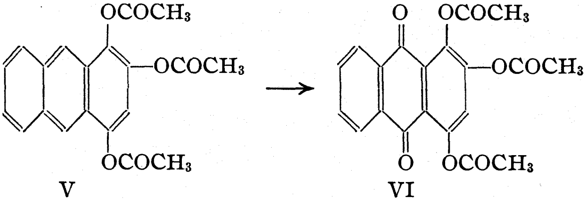
[1] (a) Fieser, THIS JOURNAL, 48, 2922 (1926); (b) 48, 3201 (1926); (c) 49, 857 (1927).

[2] Fieser, *ibid.*, 50, 439 (1928).

[3] Lagodzinski. Ann., 342, 59 (1905).

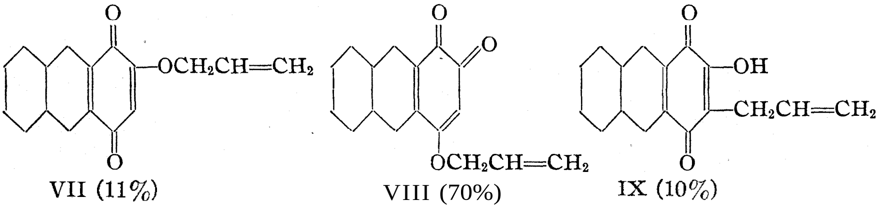
The structure of this hydroxyanthraquinone was established by oxidizing its hydroquinone triacetate, 1,2,4-triacetoxy-anthracene (V), with chromic



acid. The resulting substance was found to be identical with a sample of triacetylpurpurin, VI, prepared from purpurin.

2-Hydroxy-1,4-anthraquinone resembles the corresponding naphthoquinone to a marked degree. The only noteworthy difference between the two substances is that the former does not form a bisulfite addition product and, therefore, unquestionably has the *p*-quinonoid structure. The compound, which crystallizes in yellow needles, displaces even acetic acid from solutions of its salts, it reacts readily with amines and it is esterified by methyl alcohol in the presence of mineral acids to give II. This ether, together with 4-methoxy-1,2-anthraquinone, is produced in the ratio of 33% of the former to 62.5% of the latter by the action of methyl iodide on the silver salt of 2-hydroxy-1-4-anthraquinone. The isomers exhibit all of the properties characteristic of the corresponding methoxynaphthoquinones;[1a] the o-quinone ether, for example, forms a soluble bisulfite compound and is converted into the isomer by the action of methyl alcohol and hydrogen chloride.

Allyl bromide reacts with the silver salt of 2-hydroxy-1,4-anthraquinone with the formation of three isomers in the proportions indicated.



According to views previously expressed,[1a,b] VII is the result of simple methathesis, VIII is produced as a result of the 1,4-addition of the alkyl halide, while IX, which can also be prepared by the rearrangement of VIII, here results from the 1,2-addition of the alkyl halide. The relative yields of the isomers are very nearly the same as in the allylation of hydroxynaphthoquinone, and this is also true of the results of methylation.

All of these facts indicate that the presence of the additional benzene ring is of little consequence; the dominant feature in the structures of these hydroxy quinones of the naphthalene and anthracene series is the grouping, $O{=}\overset{|}{C}{-}CH{=}\overset{|}{C}{-}OH$, which, as Claisen first observed,[4] is almost equivalent to a carboxyl group.

The normal reduction potentials of some of the quinones here described are given in Table I. The determinations were carried out by electrometric titration of the quinone with titanous chloride or of the catalytically prepared hydroquinone solution with an oxidizing agent according to a procedure previously described.[2] Solvent "C" was employed in the cases noted because, being essentially neutral, it does not cause hydrolysis of the o-quinone ether. ΔE_1 and ΔE_2 indicate the slope of the titration curve; the theoretical value is 17.8 mv.

TABLE I

REDUCTION POTENTIALS AT 25°

Solvents: A, 0.1 N HCl; B, 50% alcohol, 0.1 N in HCl and 0.2 N in LiCl; C, 37% alcohol, 0.047 M in KH_2PO_4 and 0.047 M in Na_2HPO_4.

Compound	Solvent	Titrated with	E_0, v.			ΔE_1, mv.	ΔE_2, mv.	E_0 (av.)
2-Hydroxy-1,4-anthraquinone	B	$TiCl_3$	0.275	0.275		18.5	18.2	0.275
2-Methoxy-1,4-anthraquinone	C	$K_4Fe(CN)_6$	.272	.273		19.0	19.4	.272
4-Methoxy-1,2-anthraquinone	C	$K_4Fe(CN)_6$	,347	.345	0.346	18.8	18.5	.346
1-Methyl-5,6-(P,P-naphtho)-3,4-coumarane-quinone	B	$TiCl_3$	.304	.306	.304	18.1	17.9	.305
1,2-Anthraquinone-4-sulfonic acid	A	$TiCl_3$	.530	.530		18.6	18.2	.530
1,2-Anthraquinone	..	....	....	....	....	....	....	.490[5]
1,4-Anthraquinone[6]	B	$TiCl_3$	,401	.404	.399	17.4	17.8	.401

In Table II is given a comparison of these values with the normal potentials under similar conditions of the corresponding naphthoquinones.

TABLE II

DIFFERENCE IN POTENTIAL BETWEEN α- AND β-NAPHTHOQUINONES AND α- AND P-ANTHRAQUINONES IN MILLIVOLTS

Substituent	None	OH	OCH_3	SO_3H	$—CH_2CH(CH_3)O—$
a-Quinones	82	81	81	...	...
β-Quinones	89	..	87	98	101

The a- and β-anthraquinones are lower in potential than the similarly constituted naphthoquinones by from 81 to 101 mv., which, considering that seven pairs of compounds of different types are compared under a variety of solvent conditions, represents a fairly constant quantity and is suggestive of some fundamental relationship.

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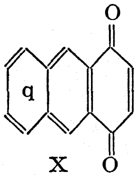
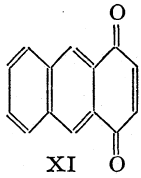
[4] Claisen, *Ann.*, 281, 306 (1894); 291, 35 (1896); *Ber.*, 59, 152 (1926).

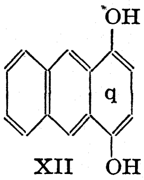
[5] Conant and Fieser, THIS JOURNAL, 46, 1858 (1924), determined this value for 95% alcohol 0.5 N in HCl.

[6] The sample was prepared according to Dienel, *Ber.*, **39, 931** (1906).

If the para-bond structure is disregarded, there are two possible formulas for a compound'such as 1,4-anthraquinone. Formula X does not explain


X


XI


XII

the observed relationship because it contains an o-quinonoid nucleus which should render the substance more, rather than less, reactive than α-naphthoquinone, in which a stable benzene ring is fused to the P-quinone group. It is not easy to judge of the properties of a compound possessing the structure of XI, but it does not seem at all likely that the substance would be any less reactive than α-naphthoquinone. Thus it does not appear that the difference in the potentials of these bi- and tricyclic quinones is connected with the structures of these quinones and an explanation must be sought by considering the structures of the reduction products.

In terms of the o-quinonoid theory of the structure of anthracene, XII should possess an added reactivity as a result of its o-quinonoid nucleus and it should be, in this respect, comparable with 9,10-anthrahydroquinone. This would mean that the corresponding quinone should have a lower reduction potential than quinones which are similar to it but which do not pass into anthracene derivatives on reduction, and this is, indeed, the case. The low reduction potential of 9,10-anthraquinone has been attributed to this same factor[7] and it is interesting to see how the potentials of the two *p*-quinones of the anthracene series compare. 9,10-Anthraquinone differs from 1,4-anthraquinone essentially in that both of its quinonoid linkages are members of benzene rings, while with the isomer only one linkage is so involved. The same relationship exists between a-naphthoquinone and *p*-benzoquinone, and the difference in their potentials is 0.224 v. It would be expected, then, if the quinone structures are of relatively little significance, that 1,4- and 9,10-anthraquinone would differ in potential by about this same amount, and the actual difference, 0.246 v., is not far from this value. This seems to establish the correctness of the interpretation adopted, namely, that 1,4-anthraquinone is comparable with 1,4-naphthoquinone and that its reduction product is comparable with 9,10-anthrahydroquinone. The o-quinonoid formula, X, hardly expresses the similarity to α-naphthoquinone, while, if Formula XI is adopted, it must be considered that the compound has at least no **very** pronounced added reactivity as a result of the tetraketone structure.

Regarding the question of the possible tautomerism of 2-hydroxy-1,4-

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[7] Fieser and Ames, THIS JOURNAL, 49, 2604 (1927).

anthraquinone, the chemical properties of the substance clearly show that the less stable β-anthraquinone form must be present in only a very small concentration in the equilibrium mixture, though it is necessary to consider that this form is capable of at least transitory existence. Assuming that the difference in potential of the two tautomers is equal to the difference in the potentials of the corresponding ethers, the constant of the tautomeric equilibrium may be calculated with the use of the equation previously developed.[2] It is found that $K = 316$, which means that 99.7% of the substance is present at equilibrium in the α-anthraquinone form. It is clear that the chemical and electrochemical evidence are in good agreement with each other, and that in this respect, also, the bi- and tricyclic quinones are very similar.

Experimental Part

1,2-Anthraquinone-4-sulfonic Acid.—A slight modification of the usual procedure* for the reduction of sodium anthraquinone-β-sulfonate greatly shortened the time required for the operation. A mixture of **150** g. of this salt,[9] **90** g. of zinc dust, 800 cc. of ammonia solution (sp. gr. **0.90**) and **350** cc. of water was placed in a flask equipped with a reflux condenser and a mechanical stirrer. The mixture was warmed on the water-bath to such a temperature that only slight frothing occurred, the temperature being increased as reduction proceeded. After about four hours reduction was complete and the precipitated product was separated from the brown filtrate while the latter was still hot. By suspending the precipitate in **3** liters of water and allowing the zinc to settle to the bottom, the greater part of the metal could be separated mechanically and the sodium anthracene-β-sulfonate obtained was suitable for conversion into β-anthrol. For this purpose the anthracene sulfonate from **200** g. of the quinone was fused with **900** g. of potassium hydroxide according to the directions of Lagodzinski;[3] yield, **80–90** g.

The 1,2-anthraquinone[10] prepared in the manner described by Lagodzinski was found to contain considerable inert material which is not easily removed on a large scale, but which does not greatly interfere with the reaction of the quinone with sodium bisulfite. The quinone obtained from **60** g. of β-anthrol, while still moist, was made into a paste with **500** cc. of water, **35** g of sodium bisulfite was added and the mixture was stirred mechanically for two hours. The quinone rapidly dissolved while a fine

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[8] Liebermann, **Ann.,** 212, **57 (1882).**

[9] I am indebted to the E. I. du Pont de Nemours & Co. for a large supply of this material.

[10] Attempts to convert this quinone into a dihydroxy derivative by the action of calcium oxychloride, following the methods employed for the preparation of isonaphthazarin, were unsuccessful. In no case was there any evidence of the formation of such a quinone; the sole product isolated. separated from considerable black material by extraction with dilute hydrochloric acid, was a colorless acid, very readily soluble in water and melting at 232°. It is probably the lactone acid,  $C_{10}H_6\begin{array}{l}\diagup\\ \diagdown \mathrm{CHCHOHCOOH}\end{array}$, corresponding to the oxidation product of β-naphthoquinone obtained by Zincke, *Ber.*, 25, **405 (1892).**

Anal. Calcd. for $C_{14}H_{10}O_5$: C, **65.11;** H, **3.91.** Found: C, **65.33;** H, **3.80.**

suspension of black material remained unaltered. The mixture was then warmed to the boiling point and a solution of 25 cc. of sulfuric acid in 80 cc. of water was slowly added. A few drops of caprylic alcohol served to prevent foaming due to the evolution of sulfur dioxide. The hot solution was filtered through a large folded paper and to the dark brown filtrate, after cooling to room temperature, was added a solution of 21 g. of chromic acid in a small volume of water. The solution became deep red in color and, after adding 200 cc. of saturated sodium chloride solution, the sodium salt of 1,2-anthraquinone-4-sulfonic acid separated in the form of a fine, crystalline powder. It was washed with dilute sodium chloride solution and dried at 120°; yield, 50 g. (52%, based on the weight of β-anthrol). When pure 1,2-anthraquinone was employed for this reaction instead of the crude material, the yield of the sulfonate, which was isolated in the form of the ammonium salt in the manner described below, was 74% of the theoretical quantity.

The sodium salt is readily soluble in water and crystallizes in the form of small, dark red needles.

Anal.[11] Calcd. for $C_{14}H_7O_5SNa$: Na, 7.41. Found: 7.27.

Neutral solutions of this compound do not undergo decomposition as readily as is the case with β-naphthoquinone sulfonate, but the substance is rapidly converted into brown products in the presence of alkali. The quinone forms a colorless bisulfite addition product and readily reacts with aromatic amines to give red, alkali-soluble anilino-quinones.

The ammonium salt was obtained by adding an excess of saturated ammonium nitrate solution to a solution of the sodium salt in hot water. The two salts are easily distinguished, for, when each is precipitated by salting out, the sodium derivative separates in the form of a bright red suspension which is very difficult to filter and dry, while the ammonium salt forms a compact, dull red precipitate. The conversion is nearly quantitative when the sodium salt employed is pure; the crude material described above apparently contained considerable sodium chloride for it yielded only 58% of the theoretical quantity of the ammonium salt. The ammonium sulfonate dissolves readily in alcohol or water but the solutions rapidly undergo decomposition. Crystallized from a dilute ammonium nitrate solution, it formed small, dark red prisms.

Anal.[11] Calcd. for $C_{14}H_{11}O_5NS$: S, 10.50. Found: 10.14.

The β-anthraquinone sulfonate was also obtained from nitroso-β-anthrol, though the process was less satisfactory than that given above. The nitroso compound, in the form of its sodium salt, was treated with a solution of sodium bisulfite (2 molecular equivalents), the solution was filtered from a rather considerable quantity of black material, and a large excess of sulfuric acid was added. After standing at 30–40° for one week, the separation of yellow crystals of 1-amino-2-anthrol-4-sulfonicacid had ceased, the yield being 10–15% of the theoretical. The low yield is probably due both to a partial destruction of the nitroso compound by the bisulfite and to incomplete reduction of the intermediate product by sulfur dioxide. The sulfonic acid derivative, which is insoluble in water, crystallized from 10% bisulfite solution in the form of yellow needles containing combined water which was not eliminated on drying in *vacuo* at 100°.

Anal.[11] Calcd. for $C_{14}H_{11}O_4NS\ {}^1/_2H_2O$: S, 10.75. Found: 10.49.

On stirring this compound into 25% nitric acid, oxidation rapidly took place and crystallization of ammonium 1,2-anthraquinone-4-sulfonate occurred.

2-Hydroxy-1,4-anthraquinone.—To a suspension of 10 g. of β-anthraquinone ammonium sulfonate in 100 cc. of methyl alcohol, 15 cc. of concd. sulfuric acid was

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[11] Analysis of Dr. F. H. Case.

slowly added while the mixture was well shaken. The salt rapidly dissolved, the solution warmed and became deep red in color, sulfur dioxide was given off and suddenly a yellow substance separated and the flask was soon filled with a thick, crystalline paste. After allowing the mixture to cool, the product was collected and washed well with methyl alcohol. Addition of water to the filtrate causes the precipitation of only a negligible quantity of impure material. The yellow product, 2-methoxy-1,4-anthraquinone (see below), was nearly pure; yield, 6.6 g. (85%). It was boiled with 600 cc. of water and 5 cc. of 6 *N* sodium hydroxide solution until most of the material had dissolved, the orange-yellow solution was filtered and the residue boiled with sufficient dilute alkali to dissolve it. The sodium salt of hydroxyanthraquinone was precipitated by adding 15 cc. of 6 N alkali to the combined filtrates. It separated from the solution while still hot in the form of a red powder. On acidifying the solution of this salt in boiling water, 2-hydroxy-1,4-anthraquinone separated in the form of very slender, bright yellow needles, and in very pure condition; yield, 5.7 g. (92%).

2-Hydroxy-1,4-anthraquinone is moderately soluble in glacial acetic acid or in alcohol, sparingly soluble in benzene, ether or water, and dissolves only to a very slight extent in bisulfite solution. The solution in concd. sulfuric acid is claret red, the sodium hydroxide, carbonate or acetate solution is pale orange-yellow, while the vat is orange-red. The substance condenses with aromatic amines in glacial acetic acid solution to give alkali-insoluble anilino-quinones. It crystallizes from toluene or glacial acetic acid in the form of yellow needles which melt with decomposition at 243°, a red color being imparted to the glass capillary even above the point of fusion.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.99; H, 3.60. Found: C, 74.81; H, 3.76.

The sodium salt, prepared as described above and crystallized from water, formed orange micro-needles which dissolve readily in water but which are very sparingly soluble in dilute sodium hydroxide solution.

Anal. Calcd. for $C_{14}H_7O_3Na$: Na, 9.35. Found: 9.36.

The silver salt was prepared by precipitation from a solution of the ammonium salt at 60°; the material was at first gelatinous but in a few seconds it changes into a crystalline, dark red powder.

Anal. Calcd. for $C_{14}H_7O_3Ag$: Ag, 32.59. Found: 32.42.

The acetyl derivative was obtained by the action of acetic anhydride and a small quantity of concd. sulfuric acid on the quinone. Crystallized from alcohol, in which it is sparingly soluble, or from benzene, which readily dissolves the material, it forms yellow plates melting at 195°.

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.17; H, 3.79. Found: C, 72.02; H, 3.86.

1,2,4-Triacetoxy-anthracene was prepared by boiling for ten minutes a mixture of 2 *g.* of the hydroxyanthraquinone, 5 g. of sodium acetate, **6** *g.* of zinc dust and 40 cc. of acetic anhydride. The solution was filtered while hot, the residue washed with hot glacial acetic acid and water was added to the hot filtrate. The acetyl derivative separated in crystalline form and in nearly quantitative yield. It is moderately soluble in benzene or glacial acetic acid, and the solutions, particularly when dilute and when viewed in thin layers, exhibit pronounced blue fluorescence. It is best crystallized from benzene-ligroin, forming colorless needles; m. p. 191".

Anal. Calcd. for $C_{20}H_{16}O_6$: C, 68.16; H, 4.58. Found: C, 68.06; H, 4.62.

On boiling a solution of 1 g. of this anthracene derivative in glacial acetic acid with 0.8 g. of chromic acid for five minutes, adding a little water and cooling, triacetyl purpurin was obtained. After repeated crystallization from alcohol, the melting point of the yellow needles remained constant at 202–203°, and no depression of the melting point was produced on admixture of a sample of the triacetyl derivative (m. p. 202–203°) prepared from purpurin. Schunck and Roemer[12] report a melting point of 198–200°.

Anal. Calcd. for $C_{20}H_{14}O_8$: C, 62.82; H, 3.69. Found: C, 62.75; H, 3.85.

Methylation

A mixture of 4 g. of 2-hydroxy-1,4-anthraquinone silver salt, 2 g. of methyl iodide and 40 cc. of benzene was shaken mechanically until the red salt had disappeared (about ten hours), and the product was then extracted with benzene and the solvent evaporated under diminished pressure. The finely-powdered material was first triturated with ammonia solution to remove a small quantity (0.14 g.) of the hydroxy compound and then with successive portions of bisulfite solution to remove the o-quinone isomer formed. This was precipitated from the solution by the addition of sodium carbonate; yield, 1.71 g. (62.5% of the theoretical amount, allowing for the hydroxy compound recovered); m. p., 197°. The residue insoluble in bisulfite solution was the somewhat impure p-quinone ether; yield, 0.9 g. (33%).

4-Methoxy-1,2-anthraquinone.—Crystallized from benzene, in which it is moderately soluble, the compound formed clusters of fine, yellow needles melting at 198°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.52; H, 4.48.

The ether dissolves readily in bisulfite solution, gives a claret-red solution in concd. sulfuric acid, and is readily hydrolyzed by boiling with dilute alcoholic hydrochloric acid or with alkali. On boiling for a short time a solution of the substance in methyl alcohol containing a small quantity of concd. sulfuric acid it is completely converted into the isomeric p-quinone ether.

2-Methoxy-1,4-anthraquinone.—The material obtained directly from ammonium β-anthraquinone sulfonate is nearly pure but contains a trace of a dark-colored by-product which is best removed by crystallization from toluene with the use of animal charcoal. Small, yellow needles melting at 217° are thus obtained.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.61; H, 4.23. Found C, 75.54; H, 4.53.

This ether is moderately soluble in benzene, toluene or glacial acetic acid, insoluble in bisulfite solution, and it dissolves without change in concd sulfuric acid with a claret-red color. It is not readily hydrolyzed by dilute alcoholic hydrochloric acid. The material prepared in the above manner was compared with samples obtained by esterifying hydroxyanthraquinone with methyl alcohol and hydrogen chloride and by methylation with methyl iodide. The substances were identical.

Allylation

Three products are formed in the reaction of hydroxyanthraquinone silver salt with allyl bromide and they may be readily separated by taking advantage of the solubility of the o-quinone ether in bisulfite solution and of the acidic nature of the C-alkyl derivative. A mixture of 8.9 g. of the silver salt, 150 cc. of benzene and 3.5 g. of allyl bromide was boiled for one-half hour and the silver bromide separated. Most of the o-quinone ether crystallized from the filtrate; the mother liquor, diluted with ether, was extracted with ammonia solution and then with bisulfite solution and the products were recovered in the usual way. From the mother liquor, dried and concentrated, the *p*-quinone ether was obtained by the addition of petroleum ether; it was somewhat dark in color but melted only a few degrees below the correct temperature. The other isomers were nearly pure. Yields: *o*-quinone ether, 4.9 g. (70%); p-quinone ether, 0.8 g. (11%); C-alkyl derivative, 0.7 g. (10%).

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[12] Schunck and Roemer, Ber., 10, 553 (1877).

4-Alloxy-1,2-anthraquinone.—This compound is best crystallized from benzene, in which it dissolves readily; it separates in the form of flat, yellow needles; m. p. 173". It readily undergoes rearrangement, as indicated below.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.22; H, 4.78.

2-Alloxy-1,4-anthraquinone.—In order to remove dark-colored by-products it was necessary to precipitate the crude material several times from its solution in glacial acetic acid by the addition of water; the ether was then crystallized repeatedly from benzene-ligroin and obtained in the form of light yellow blades melting at 139°.

And. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.28; H, 4.67.

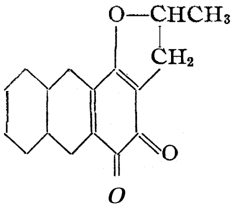
2-Allyl-3-hydroxy-1,4-anthraquinone.—This compound dissolves readily in glacial acetic acid and crystallizes from this solvent in the form of beautifully lustrous, flat, yellow needles melting at 215°. It is readily soluble in benzene, moderately soluble in alcohol, and the alkaline or alkali carbonate solution is orange in color.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 76.90; H, 4.68.

The same substance is easily obtained by the rearrangement of 4-alloxy-1,2-anthraquinone. Three and one-half g. of the ether was heated in an oil-bath maintained at 175°. As soon as fusion was complete the temperature of the melt rose rapidly to 220° and the vessel was at once removed from the oil-bath. The melt quickly solidified and now failed to fuse at 175". The product was extracted with ammonia solution and crystallized once from alcohol; yield, 3 g.; m. p. 214°.

1-Methyl-5,6-(β,β-naphtho)-3,4-coumaranquinone.—One g. of allylhydroxyanthraquinone was dissolved in 7 cc. of concd. sulfuric acid and after one-half hour the claret-red solution was poured into water. The somewhat oily, red precipitate was dissolved in bisulfite solution and recovered by acidification of the solution, when it separated in crystalline condition. After several crystallizations from benzene-ligroin the melting point remained constant at 186–187°, and small, orange-red needles were obtained.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.01; H, 4.85.



This coumaran derivative is attacked only very slowly by dilute alkali in the cold but on warming it is rapidly dissolved, giving an orange-red solution from which acids precipitate a yellow substance in crystalline condition The compound crystallizes from benzene, in which it is only moderately soluble, in the form of small, yellow needles, m. p. 211–212°. The acidic character and the color of the material, together with the analysis, indicate the structure of **2-(β-hydroxypropyl)-3-hydroxy-1,4-anthraquinone.**

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.05; H, 5.34

Summary

2-Hydroxy-1,4-anthraquinone has been prepared and its structure established by conversion into triacetylpurpurin. The silver salt of this quinone reacts with a saturated alkyl halide to give a mixture of the products of metathesis and of 1,4-addition, while with allyl bromide a C-alkyl derivative, the product of 1,2-addition, is also formed. These and other results show that the properties and reactions of 2-hydroxy-1,4-anthraquinone are strikingly similar to those of 2-hydroxy-1,4-naphthoquinone.

The reduction potentials of α- and β-anthraquinones are from 81 to

101 mv. lower than those of the corresponding naphthoquinones, while α-anthraquinone is 246 mv. higher in potential than 9,10-anthraquinone. These facts are consistent with the conception that a-anthraquinone is in every way comparable to a-naphthoquinone, but that its reduction product should be compared with 9,10-anthrahydroquinone.

Bryn Mawr, Pennsylvania

[Contribution from the Department of Chemistry of Mount Holyoke College]

THE ISOMERISM OF PHENYLPHTHALIMIDE AND A STUDY OF THE NITRO AND CHLORO DERIVATIVES

By Mary L. Sherrill, Florence L. Schaepfer and Elizabeth P. Shoyer

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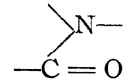
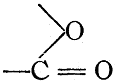
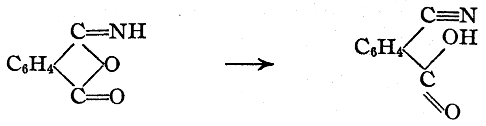
A critical study of the extensive work which has been done on phenylphthalimide or phthalanil, and its derivatives shows not only conflicting theoretical interpretations but contradictory experimental results. In addition to the closely related compounds the phthalanils, the phthalanilic acids, and the phthalamides which have not always been completely separated from one another, there are the two isomeric phthalimides—the symmetrical type —C = O and the asymmetrical type —C = N—





These isomers differ so slightly in their physical and chemical properties that the separation and identification have been difficult and this accounts for much of the confusion and inaccuracy in the reported results. In the present study a complete survey of the literature was made and much of the experimental work repeated, duplicated in some cases and in the case of disputed points additional evidence has been obtained. The more general methods of preparation of the phthalanils and the phthalanilic acids have not been a matter of controversy, but this is not true of the preparation and isolation of the isomeric phthalanil derivatives.

The first evidence of the existence of an isomeric phthalimide was reported by Hoogewerff and van Dorp.[1] They found that o-cyanobenzoic acid was obtained by the action of ammonia on phthalyl chloride. Since neither phthalimide nor the phthaldiamide can be transformed by ammonia into the o-cyanobenzoic acid, they assumed the formation of an asymmetrical phthalimide as an intermediate compound—this evidently was unstable in alkaline solution and rearranged to the acid, thus



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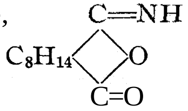
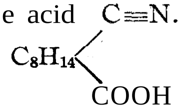
[1] Hoogewerff and van Dorp, *Rec. trav. chim.*, **11, 84 (1892).**

A year later the same authors[2] prepared compounds isomeric with the substituted camphorimides by treating the proper camphoramic acid with acetyl chloride or phosphorus oxychloride. These camphor-iso-imides were found to react with ammonia to give the corresponding cyano acid and therefore were assumed to have the following structure,  giving the acid  Iso-imides of other dicarboxylic acids could not be prepared but the iso-imide of phthalic acid was evidently obtained although not in a pure state; the substance obtained did give, with ammonia, o-cyanobenzoic acid. This work was one of the most important proofs of the existence of iso-imides and of the asymmetrical structure of the compounds obtained by the action of acetyl chloride on a dibasic acid. It stimulated interest in the preparation of various substituted iso-imides and phthalmethyl-iso-imide and phthalbenzyl-iso-imide were prepared in this way.[3] These iso-imides were crystalline products whose melting points were much lower than those of the ordinary imides; they were bases, but the salts were easily decomposed in the presence of water forming the corresponding acid. In 1896 van der Meulen,[4] working in the same laboratories, prepared the phthalphenyl-iso-imide by the action of acetyl chloride on phthalanilic acid. He isolated a crystalline compound which melted at 115–117°, while the melting point of the ordinary phenylphthalimide was 208°. These results were duplicated by other investigators.[5] Van der Meulen[6] found that when iso-imides were heated they were converted into the ordinary imides, that alcohols transformed them and their hydrochlorides into amidoic esters, sometimes into iso-esters and that amines formed with the iso-imides di-amides.

In 1901 Kuhara and Fukui[7] claimed to have prepared a substance isomeric with phthalanil which they called a-phenylphthalimide. This work was repeated by Kuhara and Komatsu;[8] the a-phenylphthalimide, however, was not isolated but normal phenylphthalimide, phthaldiphenyl-

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[2] Hoogewerff and van Dorp, *Rec. trav. chim.*, 12, 12 (1893).

[3] Hoogewerff and van Dorp, *ibid.*, **13,** 93 (1894).

[4] Van der Meulen, *ibid.*, 15,282 (1896).

[5] (a) Hoogewerff and van Dorp, *ibid.*, 21, 339 (1901); (b) Pummerer and Dorfmüller, Ber., 45, 292 (1912).

[6] Van der Meulen, *Rec. trav. chim.*, 15, 323 (1896).

[7] Kuhara and Fukui, Am. *Chem.* J.,26,454 (1901).

[8] Kuhara and Komatsu, *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.*, 1, 391 (1908); 2, 365 (1909–1910).

diamide and a hydrated di-amide were obtained. Then these investigators repeated the work of van der Meulen[4,6] and reported that they could not duplicate his work. They obtained two substances isomeric with phthalanil; one, yellow in color, they called the iso-imide; the other, white in color, they designated as β,α-phenylphthalimide.

Since the work of Kuhara is the last publication dealing with these isomers of phthalanil, his conclusions and results have remained unchallenged. A study of his methods seemed to indicate that the two isomers he reported were mixtures, so it was thought advisable to repeat the experiments of van der Meulen, Hoogewerff and van Dorp, Pummerer and Dorfmuller on the one hand and those of Kuhara, Fukui, Komatsu on the other, in order to prove as far as possible the existence or nonexistence of the various isomers mentioned above. Especial attention was given to the preparation of van der Meulen's phthalphenyl-iso-imide and to the preparation and isolation of the β,α-phenylphthalimide and the isomeric phenylphthalimide reported by Kuhara.

Early in the work in this Laboratory it was found that phenylphthalimide and phthalanilic acid could be completely separated from each other by a difference of solubility in chloroform. By this method it was found that a compound reported by Gabriel and Thorpe[9] as phthalanilic acid (m. p. 192°) was a mixture of phenylphthalimide (m. p. 208°) and phthalanilic acid (m. p. 169°, decompd.). It was found possible by the use of chloroform to separate phenylphthalimide from phthaldiphenyldiamide and thus some very clean cut separations were made possible. The results show that van der Meulen's phthalphenyl-iso-imide is the true isomer of phthalanil, that the iso-phthalanil of Kuhara and Fukui, designated as a-phenylphthalimide, is a mixture of phthaldiphenyldiamide, that the β,α-phenylphthalimide of Kuhara is a mixture of phthalphenyl-iso-imide and phthalanilic acid and that the yellow product obtained by Kuhara (m. p. 125–126") was a mixture of the true isophthalanil (m. p. 116°) and small amounts of *n*-phthalanil.

The literature showed also some conflicting data with regard to the o-m-p-nitrophthalanils and indicated that investigation of some of the methods might prove of value. Accordingly, the work of various investigators, including Pawlewski, Dobreff and Kuhara was repeated in this Laboratory with the result that much of the confusion has been eliminated. The p-chlorophthalanilic acid and the *p*-chlorophthalanil[10] have been prepared but no reference is given in the literature to the corresponding *ortho* and *meta* compounds. These compounds, as well as the para compounds, have been prepared in this work.

[9] Gabriel and Thorpe, Ber., 11, 2260 (1878).

[10] (a) Tingle and Brenton, THIS JOURNAL, 31, 1157 (1909); (b) Gabriel, *Ber.*, 11, 2261 (1878).

Experimental

Phthalanilic acid was prepared[11] by the reaction of chloroform solutions of phthalic anhydride (50 g.) and aniline (31.4 g.). There was considerable heat of reaction and the white phthalanilic acid which precipitated out was found to be practically pure; it melted at 169° with evolution of steam, the residue resolidified and remelted at 207°, the melting point of phthalanil.

The effect of alcohol on phthalanilic acid has been studied[12] and the final product has been proved to be phthalanil. In this process, however, the alcohol solutions become yellow and this color has not been definitely accounted for. Since one of the isomers of phthalanil is yellow,[6] it was thought that some of the isomeric compound might be formed as an intermediate. A series of experiments was carried out in which the action of alcohol (95% and absolute) on the acid was studied. The concentration, temperature, length of contact and light conditions were varied. The color of the solution increased from pale yellow to a deep red directly as there was an increase in the temperature, in the concentration of the solution, in the length of time of reaction and in the volume of air above the solution. The results seemed to indicate a slow oxidation and the change was most rapid and extensive in the presence of an oxidizing agent, as shown by the addition of a small amount of hydrogen peroxide to the solution. No trace of the isomer could be obtained. The products isolated after the reaction were only phthalanilic acid and phthalanil, the quantity of the latter increasing with the time. The ultraviolet absorption spectra of alcoholic solutions of phthalanil and phthalanilic acid were also investigated and showed that even very dilute solutions of phthalanilic acid were gradullay transformed into phthalanil.

Phthalanil was prepared by the fusion of phthalic anhydride (50 g.) with aniline at a temperature of 250–260°.[13] The product was washed with alcohol, dissolved in chloroform and precipitated by alcohol in the form of glistening white needles (m. p. 207°). On account of the extreme solubility of phthalanil in chloroform and the complete insolubility of phthalanilic acid in this solvent it was found possible to make a complete separation of the two and the method was used throughout this investigation. There is no indication in the literature that chloroform would serve for this separation. Repetition of the work of Gabriel and of Thorpe[9,14] showed that the product they obtained of melting point 192°, thought to be pure phthalanilic acid, could be separated into pure phthalanil (m. p. 207") and pure phthalanilic acid (m. p. 169°) by extraction with chloroform.

[11] Anschütz, Ber., 20,3214 (1887).

[12] Tingle, THIS JOURNAL, 30, 1882 (1908).

[13] Laurent and Gerhardt, Ann., 68, 34 (1848).

[14] Thorpe, Ber.. 26, 1262 (1893).

Isomeric **Phthalanils**

The fundamental reaction involved in the preparation of the iso-imides[2] consisted in the action of acetyl chloride on phthalamic acid. Therefore, before any duplication of the methods used by previous investigators was undertaken, this reaction was carried out under varying conditions of time and temperature and a careful separation and identification of the products were made. A pale yellow product (melting between 160 and 203°) resulted from the action of acetyl chloride on phthalanilic acid either at ordinary temperature or at 40°. If the yellow product was allowed to stand in the air or dried at a temperature of 80°, the yellow color disappeared entirely. If, however, the product was dried in a vacuum desiccator and then kept in an atmosphere of carbon dioxide, the yellow color persisted for several weeks. The reaction product was extracted with ether and the ether extract gave a white crystalline substance melting with decomposition between 157 and 202°. By extraction of this substance with chloroform, phthalanil was isolated (m. p. 207°), phthalanilic acid (m. p. 169°) was obtained and some phthalic acid, colorless plates (m. p. 184° with decomposition forming phthalic anhydride, m. p. 129–130°). The identification of these substances was checked by comparison with the pure substance; in each case mixed melting points showed no depression. The phthalic acid was further identified by the fluorescein test; phthalanil and phthalanilic acid gave negative tests under the same conditions. The residue left after the ether extraction was treated with chloroform, which removed a small amount of phthalanil and the residue melted at 237° with decomposition. This proved to be the phthaldiphenyldiamide,[6,5a,15] for when heated with glacial acetic acid it was transformed into phthalanil. These results show that the yellow product contained the hydrochloride of phthalphenyl-iso-imide. This hydrochloride was unstable in the air (more stable in dry air or in carbon dioxide), giving off hydrogen chloride and leaving the iso-imide. This iso-imide has been shown to be easily transformed into phthalanil.[5b] The presence of phthalic acid indicated the decomposition of some of the phthalanilic acid into phthalic acid and aniline. The reaction of aniline with the phenyl-iso-imide would account for the small amount of diamide formed.

An effort was made to prepare the α-phenylphthalimide of Kuhara.[7] The work was repeated in every detail, as follows. To an ethereal solution of 93 g. of aniline cooled to —10°, an ethereal solution of 50.75 g. of phthalyl chloride, also cooled to —10°, was added drop by drop. The temperature was kept below —6°. Hydrogen chloride was evolved and a white precipitate separated. The reaction mixture was kept in a freezing mixture for two hours. The precipitate was filtered and washed suc-

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[15] Rogow, *Ber.*, **30, 1442 (1897).**

cessiuely with hydrochloric acid, ammonia and water, as described by Kuhara. The product obtained melted at 215–219°. A chloroform extraction separated a very small amount of phthalanil (m. p. 207°); the main portion of the material was insoluble in chloroform and slightly soluble in alcohol. By recrystallization from alcohol a white crystalline product was obtained, m. p. 231° with decomposition. This was soluble in hot glacial acetic acid but was thereby converted into phthalanil and was therefore phthalanilide. This confirms the work of Hoogewerff and van Dorp,[5a] Chambers,[16] and Dunlap and Cummer,[17] who found that ethereal solutions of aniline and phthalyl chloride at low temperature formed, in the main, phthalanilide. Therefore, the original product, m. p. 215–219°, proved to be a mixture of n-phthalanil and phthalanilide and not an isomeric phthalanil.

Phthalphenyl-iso-imide, m. p. 116°, was prepared by careful duplication of the work of van der Meulen.[4] Five grams of phthalanilic acid was treated with 30 g. of acetyl chloride and the mixture heated at a temperature of 60° for seven minutes; the mixture turned yellow almost immediately. The cooled mixture was treated with carbon disulfide, the insoluble hydrochloride of phthalphenyl-iso-imide was filtered and immediately transferred to anhydrous ether. The iso-imide was freed by 30% potassium hydroxide, the flask was kept cold and the potash added only to bare alkalinity. The product was then practically all dissolved and the ether solution, yellow in color, was separated from the water layer and dried over solid potassium hydroxide for ten minutes. From this solution, filtered and evaporated in a desiccator over sulfuric acid, yellow needle crystals (m. p. 112–115°) were obtained. After one recrystallization from anhydrous ether, the crystals melted at 116°. This agreed with the results of van der Meulen[4] and Pummerer and Dorfmüller[5b] although Hoogewerff and van Dorp[5a] gave the melting point as 120–122°. Kuhara and Komatsu[S] claimed that they could not obtain the product which van der Meulen reported but that, on distillation, of part of the ether solution and then on spontaneous evaporation of the remainder phthalanil crystallized out first and then an amber-colored substance. The latter, on repeated recrystallization from anhydrous ether, gave amber-colored rhombic crystals, m. p. 125–126°. Kuhara also evaporated, as quickly as possible, the ethereal solution of the reaction product and obtained an almost colorless crystalline substance which, after one recrystallization from anhydrous ether, melted at 83–84°. This he designated as β,α-phenylphthalimide and believed both this and the amber-colored substance to be the true isomers of phthalanil rather than the yellow needles, m. p. 116°, of van der Meulen. In order to clear up these points the phthalphenyl-iso-imide was prepared as given above; a portion of the ether solution was evaporated in a desiccator over sulfuric acid and the yellow crystals, m. p. 116°, were obtained. A second portion of the same ether solution was partially distilled and then allowed to evaporate. The first product crystallizing out was phthalanil, m. p. 207"; further evaporation gave a very pale yellow residue which melted from 70–80°, resolidified and melted at 207°. A chloroform extraction of this mixture was made; the residue insoluble in chloroform proved to be pure phthalanilic acid, m. p. 169". It melted with evolution of gas, resolidified and remelted at 207°. The chloroform extract evaporated in a desiccator over sulfuric acid gave clusters of yellow needles, m. p. 116°; therefore the reaction prod-

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[16] Chambers, THIS JOURNAL, 25, 601 (1903).

[17] Dunlap and Cummer, *ibid.*, 25,612 (1903).

uct, m. p. 70–80°, was a mixture of phthalphenyl-iso-imide and phthalanilic acid. This mixture obtained on heating the ethereal solution was probably caused by traces of alkali hydrolyzing the iso-imide into the acid.

The fact that a low melting reaction product (70–80°) was obtained in this Laboratory on repetition of Kuhara's work and that this proved to be a mixture indicates definitely that what Kuhara and Komatsu really had in the case of the substance melting at 83–84°, called β,α-phenylphthalimide was a mixture of van der Meulen's iso-imide and phthalanilic acid. Further confirmation lies in the fact that whenever the phenyl-iso-imide melting at 116° was mixed with phthalanilic acid, the mixture melted between 70 and 85°. Kuhara also states that when heated by itself β,α-phenylphthalimide was converted into the normal phenylphthalimide; this would be true of a mixture of phthalphenyl-iso-imide and phthalanilic acid since, on heating, both of these substances are converted into the ordinary phenylphthalimide.

Whenever the phthalphenyl-iso-imide prepared in this Laboratory was exposed to the air, it was found that the melting point became gradually higher, due to the fact that it was slowly transformed into the normal phthalanil. It was also proved that a mixture of a small amount of phthalanil with the iso-phthalanil melted at 120–126°, which accounts for the product of higher melting point obtained by Hoogewerff and van Dorp (120–122') and that obtained by Kuhara (125–126°). When the phthalphenyl-iso-imide was allowed to stand in the presence of acid fumes, however, long, white needle crystals could be observed on the surface of the iso-imide. These were collected and found to be phthalic anhydride. The residue was found to consist of a mixture of the normal phenylphthalimide, the phthalphenyl-iso-imide and the phthaldiphenyldiamide. The two former substances were separated from the latter by extraction with ether and were then separated from each other by fractional crystallization from the ether solution.

Nitrophenylphthalimides

Preliminary to the checking of the work of various investigators on the isomeric nitrophenylphthalimides, nitro phthalanilic acids were prepared.

p-**Nitrophthalanilic** acid (m. p. 192° with decomposition) was prepared by the reaction of acetic ester solutions of *p*-nitraniline and phthalic anhydride.[18] The solvent was distilled off and the residue, after recrystallization from alcohol, gave a crystalline product which melted at 190–192° with evolution of gas, resolidified and melted again at 260° (melting point of *p*-nitrophthalanil, 262–263°). The method used in the preparation of phthalanilic acid was found to give better yields and more satisfactory material. Chloroform solutions of equimolecular quantities of p-nitraniline and phthalic anhydride were mixed and heated until the yellow color of the solution gradually faded. When cool the product was filtered, washed with cold chloroform and then recrystallized

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[18] (a) Meyer and Lüders, *Ann.*, **327**, 52 (1903); (b) *Ann.*, **415**, 29 (1917).

from hot chloroform. It formed white crystals which melted at 192°, evolved a gas, resolidified and melted at 262–263°.

m-**Nitrophthalanilic** acid (m. p. 202° with decomposition) was prepared by the reaction of acetic ester solutions of m-nitraniline and phthalic anhydride. Chloroform solutions of the reagents gave, as for the para compound, a theoretical yield and the product washed with chloroform consisted of white needles which melted at 202°, resolidified and melted at 240–242°.

o-Nitrophthalanilic acid (m. p. 149–151°) was also prepared by the action of *o*-nitraniline on phthalic anhydride in ethyl acetate solution and in chloroform solution. The acid is very soluble in both acetic ester and chloroform, so it did not precipitate out as in the case of the para and meta compounds. In order to isolate the o-nitrophthalanilic acid it was necessary to evaporate the solvent in each case to a small volume and stir until the acid crystallized. The product, washed with ether, was purified by precipitation with hydrochloric acid from a solution in sodium hydroxide. It formed yellow needles which melted at 149–151° (Meyer and Lüders[18b] give 146–148°) without evolution of gas and the liquid did not resolidify on further heating as in the case of the para and meta acids. If the melted product was cooled, however, and heated again it began to melt at 150° and water vapor came off at 200°, the melting point of the *o*-nitrophthalimides.

The normal nitrophenylphthalimides, *p*-nitrophenylphthalimide (m. p. 262–264°), m-nitrophenylphthalimide (m. p. 242–244") and o-nitrophenylphthalimide (m. p. 202–203") were prepared by the fusion of the proper nitraniline with phthalic anhydride. according to Meyer and Maier.[19] These corresponded in properties and melting points to the values given by other investigators[m] for their normal compounds, but did not correspond to the compounds reported by Dobreff.[21]

Since Kuhara, Komatsu and Nishiyori claimed to have obtained both the symmetrical and asymmetrical forms of the o-, *m*- and *p*-nitrophenylphthalimides by the reaction of ether solutions of the corresponding nitraniline and of phthalyl chloride at —10°, and since the work of van der Meulen and that done in this Laboratory showed that under these conditions the phthaldiphenyldiamides were formed, the work of Kuhara and that of Dobreff was carefully repeated.

According to Kuhara,[20c] ethereal solutions of 10 g. of *p*-nitraniline and 14.6 g. of phthalyl chloride were cooled and the chloride was added slowly to the aniline. After five minutes a precipitate gradually separated and the yellow color of the ether solution faded. The precipitate was almost white, faintly tinged with yellow. It was filtered, washed with hydrochloric acid, then with ammonia, whereupon it became deep yellow in color and some of it dissolved and then crystallized in the pores of the filter plate. It was finally washed with water and dried. Then the entire mass was extracted with alcohol. From the deep yellow alcoholic solution there crystallized first a small amount of a white substance, m. p. 262–263°. This was normal p-nitrophenylphthalimide; a mixed melting point with the pure compound showed no depression. A large quantity of this compound was obtained from the ether filtrate of the original reaction mixture. Next from the alcoholic solution a mass of fine, white needles crystallized

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[19] Meyer and Maier, Ann., 327, 42 (1903).

[20] (a) Pawlewski, Ber., 27,3430 (1894); (b) Rupe and Thiess, Ber., 42,4289 (1909); (c) Kuhara, Komatsu and Nishiyori, Mem. *Coll. Sci. Eng. Kyoto* Imp. *Univ.*, 5, 342 (1912).

[21] Dobreff, Ber., 28, 940 (1895).

which melted at 192'. This substance was reported by Kuhara to be pale yellow and to be the asymmetrical p-nitrophenylphthalimide, identical with the product obtained by Dobreff.[21] It was noted in this Laboratory, however, that the product melted with the evolution of gas, resolidified and melted again at 262–263°, which indicated that it was probably the p-nitrophthalanilic acid. It dissolved in alkalies, giving a deep yellow solution from which the acid was reprecipitated as a white powder. A mixture of this compound with p-nitrophthalanilic acid (m. p. 192°), prepared as indicated above, showed no change in the melting point. The appearance of the yellow color on washing the reaction product with ammonia was due to the formation of an ammonium salt and it was traces of this which colored the Kuhara product and that of Dobreff. This ammonium salt was obtained in this Laboratory as a yellow, crystalline product which finally crystallized from the alcohol solution.

The portion of the original reaction product insoluble in alcohol was a pale yellow powder which melted at 232° and when dissolved in hot glacial acetic acid was converted into the p-nitrophenylphthalimide. This compound was, therefore, *p*-nitrophenylphthalamide, which had been obtained by Pawlewski[22] by the action of two molecules of p-nitraniline on one molecule of phthalyl chloride. Therefore, by following the exact details of Kuhara's work, the products obtained were white *p*-nitrophenylphthalimide, m. p. 262–263°, white p-nitrophthalanilic acid, m. p. 192°, yellow *p*-nitrophenylphthalamide, m. p. 232°, and the yellow ammonium salt of *p*-nitrophthalanilic acid. When the experiment was repeated and the original reaction product washed with ether instead of hydrochloric acid and ammonia the product did not change color and from it were isolated, as above, p-nitrophenylphthalimide, p-nitrophthalanilic acid and p-nitrophenylphthalamide.

Similarly the work of Dobreff[21] was repeated. The p-nitraniline (10 g.) and the phthalyl chloride (14.6 g.) were heated on a steam-bath until the mixture changed from brown to tan. A portion of the filtered product was boiled, according to Dobreff, a long time with water and then recrystallized from alcohol. The yellow substance, insoluble in alcohol, melted at 230–232° and was p-nitrophenylphthalamide. From the alcohol solution a small amount of normal *p*-nitrophenylphthalimide (m. p. 262–263°) crystallized first, then a creamy white powder (m. p. 192" with decomposition) which proved to be the p-nitrophthalanilic acid. A second portion of the filtered product was washed with ether and extracted with alcohol and exactly the same products were obtained as from the first portion except that in this case there was much more of the normal p-nitrophenylphthalimide and much less of the p-nitrophthalanilic acid. This work showed that Dobreff's method gives largely the normal p-nitrophenylphthalimide but that boiling with water hydrolyzed this to the acid and that the 190–190.5° yellow compound of Dobreff is the p-nitrophthalanilic acid. The yellow color must have been due to traces of the yellow nitrophthalanilide.

Kuhara[23] stated that the asymmetrical nitrophenylphthalimides could be obtained by the action of acetyl chloride on the corresponding nitrophthalanilic acid but gave no details. The Hoogewerff-van Dorp method[a] was carried out with the utmost care. The p-nitrophthalanilic acid and acetyl chloride were heated for twenty minutes at 60–75°. There was no color change. The product, however, was washed with carbon disulfide, filtered and added directly to anhydrous ether. A drop or two of 30% potassium hydroxide temporarily changed the white solid into the orange potassium salt. This color disappeared, however, as long as the mixture was slightly acid. The only substance which could be isolated was the p-nitrophthalanilic acid, m. p. 192°, which was recovered practically quantitatively. Variations in temperature and time of reaction

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[22] Pawlewski, Ber., 28, 1118 (1895).

[23] Ref. 20 c, p. 346.

gave no other results. Therefore, the asymmetrical *p*-nitrophenylphthalamide cannot be prepared by the method used in the preparation of phenylphthal-iso-imide.

Kuhara[24] prepared a mono-silver salt of p-nitrophthalanilic acid from a water solution of the ammonium salt by precipitation with silver nitrate. The ammonium salt was prepared in this Laboratory by passing dry ammonia gas into an alcoholic solution of the acid. A solution of this salt was treated with silver nitrate and the silver salt, pale yellow in color, was dried and analyzed.

Anal. Calcd. for $C_{14}H_9O_5N_2Ag$: Ag, **27.46.** Found: **27.20, 27.26.**

A di-silver salt of *p*-nitrophthalanilic acid was also prepared. The di-potassium salt was first formed by the reaction of alcoholic potash on an alcoholic solution of the p-nitrophthalanilic acid. The potassium salt was washed with alcohol and dried, then dissolved in a large volume of alcohol and to this solution alcoholic silver nitrate was added. A yellow precipitate was first formed but on addition of the calculated amount of silver nitrate the precipitate became brown. This brown di-silver salt was difficultly soluble in alcohol but could be recrystallized from it.

Anal. Calcd. for $C_{14}H_{18}O_5N_2Ag_2$: Ag, **43.17.** Found: **43.20, 43.12.**

The action of phthalyl chloride on m-nitraniline according to the Kuhara method was investigated as in the case of the para compound. One product crystallizing from the alcoholic extract was white and melted at **243°.** This substance agreed in melting point and properties with the symmetrical m-nitrophenylphthalimide of other investigators.[20a,20c,22] The substance which crystallized next was m-nitrophthalanilic acid, colorless needles melting at **202"** with evolution of gas, resolidifying and melting again at 243°. This was identical with the acid previously prepared.[18b,25] A large amount of the acid was also obtained from the ether filtrate of the original reaction product. The portion least soluble in alcohol was pale yellow in color and melted at 230–232°. This was reported by Kuhara[23] as the asymmetrical m-nitrophenylphthalimide. It proved to be the m-nitrophenylphthalamide and when heated with glacial acetic acid it was converted into the asymmetrical *m*-nitrophenylphthalimide.[22]

The Dobreff method was repeated in this case too.'' The product, after being boiled with water, was crystallized from hot alcohol and found to be a mixture of *m*-nitrophenylphthalamide, m. p. 230–232°, and *m*-nitrophthalimide, **m.** p. **240–245".** This mixture was separated by treatment with chloroform; the amide was insoluble and the imide dissolved and was recrystallized from alcohol. Phthalic anhydride was obtained from the original ether solution and red crystals of the hydrochloride of *m*-nitraniline separated from the water extract. The evidence of this work shows that the yellow compound reported by Dobreff and the asymmetrical m-nitrophenylphthalimide of Kuhara were identical and were the m-nitrophenylphthalamide.

The reaction of acetyl chloride on the m-nitrophthalanilic acid was studied as in the case of the para compound, but no trace of an asymmetrical compound could be obtained. The acid was recovered practically quantitatively. At high temperatures small amounts of the symmetrical m-nitrophthalanil were obtained.

The Kuhara work[20c] on the asymmetrical o-nitrophenylphthalamide was repeated. The following products were isolated from the alcoholic solution: first colorless needles, m. p. 198–200°, which proved to be the *o*-nitrophenylphthalimide;[18b,20b,22] then yellow crystals, m. p. 149–151°, which proved to be the o-nitrophthalanilic acid, and on the sides of the beaker yellow crystals of the hydrochloride of o-nitraniline, which melted from **140–150"** with evolution of gas. The original ether filtrate when evaporated gave a yellow mixture that melted between 108–145° with evolution of a gas. This was

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[24] **Ref. 20** c, p. **362.**

[25] Tingle and Rolke, THIS JOURNAL, **30,** 1882 (1908).

extracted with dilute sodium hydroxide and from the alkali solution o-nitrophthalanilic acid was obtained. The residue, insoluble in alkali, was washed with alcohol from which yellow crystals of the hydrochloride of o-nitraniline were obtained. The residue, insoluble in alcohol, dissolved completely in chloroform and proved to be *o*-nitrophenylphthalimide. Efforts to prepare an asymmetrical o-nitrophenylphthalimide as in the case of the other nitro compounds proved unsuccessful. No trace of an isomeric compound could be obtained.

Chlorophthalanilic Acids

The *p*-chlorophthalanilic acid was prepared by the action of chloroform solutions of phthalic anhydride on p-chloro-aniline. The acid crystallized out in white needles and was filtered, washed with chloroform and found to melt at 187.5'; after cooling, it resolidified and when reheated melted at 192°, the melting point of *p*-chlorophthalanil. Recrystallization of the acid did not change its melting point. In properties it corresponded with the p-chloro acid reported by Tingle and Brenton[26] (m. p. 180°).

The m-chlorophthalanilic acid was prepared in a similar way. It formed white crystals which melted at 183–184° with evolution of gas. When cooled it resolidified and remelted at 157'. The acid is very soluble in ethyl acetate, glacial acetic acid and dilute alkalies. It can be recrystallized from alcohol, chloroform or benzene, but if prepared in chloroform solution this is unnecessary as the product is obtained pure. Since this compound is not given in the literature an analysis was made.

Anal. Calcd. for $C_{14}H_{10}O_3NCl$: N, 5.08. Found: 4.94.

The o-chlorophthalanilic acid was obtained by the same method. The acid is somewhat soluble in ether and in chloroform. It can be recrystallized from chloroform or benzene but the best product was obtained by precipitation from a solution of the acid in dilute alkali. It crystallizes in white needles, m. p. 147–148°. If it is heated to 155° a gas is gradually evolved.

Anal. Calcd. for $C_{14}H_{10}O_3NCl$: N, 5.08. Found: 4.91.

Chlorophenylphthalimides

The chlorophenylphthalimides were prepared by the fusion of the corresponding chloro-aniline with phthalic anhydride. The p-chloro compound was dissolved from the reaction mass by chloroform and precipitated by alcohol in the form of long, white. silky needles, m. p. 192°, unchanged by recrystallization from hot alcohol. It agreed in properties with the *p*-chlorophthalanil of Gabriel? The m-chlorophenylphthalimide was isolated by dissolving it in chloroform and precipitating it with alcohol. It is very soluble in chloroform, ether, benzene and ethyl acetate and insoluble in glacial acetic acid. It can be recrystallized from hot alcohol and the crystals melt at 183–184° with evolution of gas.

Anal. Calcd. for $C_{14}H_8O_2NCl$: N, 5.43. Found: 5.47, 5.39.

The o-chlorophenylphthalimide was found to be too soluble in alcohol to be precipitated by it from a chloroform solution. The residue obtained by evaporation of the chloroform solution could be recrystallized from hot alcohol. The product consisted of long, white, silky needles which melted at 132–140°. It was found to be soluble in chloroform, glacial acetic acid, benzene, ethyl acetate and ether.

Anal. Calcd. for $C_{14}H_9O_2NCl$: N, 5.43. Found: 5.34.

Attempts to prepare isomeric forms of these chlorophenylphthalimides by the action of acetyl chloride on the acids were not successful.

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[26] Ref. 10a, p. 1161.

p-Chlorophenylphthalamide was obtained by the action of *p*-chloro-aniline on phthalyl chloride. By benzene and alcoholic extraction of the reaction product, p-chlorophthalanil was recovered. The residue, insoluble in alcohol, was a white powder that melted at 233°. When it was recrystallized from hot alcohol or boiled with glacial acetic acid it was transformed into the imide. This indicates that it is the amide but because of the difficulty of getting a pure sample no analysis was made.

Summary

The results of these investigations lead to the following conclusions.

1. The phthalphenyl-iso-imide prepared by van der Meulen is the true asymmetrical phenylphthalimide. The α-phenylphthalimide of Kuhara is a mixture of phthalanil and diphenyldiamide. The β,α-phenylphthalimide (83–84°) of Kuhara is a mixture of phthalphenyl-iso-imide and phthalanilic acid. The a-phenylphthalimide (m. p. 125') of Kuhara is a mixture of the iso-imide and the normal phenylphthalimide.

2. The p-isonitrophenylphthalimide of Kuhara and of Dobreff is *p*-nitrophthalanilic acid. The m-isonitrophenylphthalimide of Kuhara and of Dobreff is a mixture of m-nitrophenylphthalamide and *m*-nitrophenylphthalimide. The o-isonitrophenylphthalimide of Kuhara is *o*-nitrophthalanilic acid with traces of o-nitrophthalanil and the hydrochloride of o-nitraniline. The asymmetrical o-, m- and *p*-nitrophenylphthalimides could not be obtained by the action of acetyl chloride on the corresponding phthalanilic acid.

3. The o-, m- and *p*-chlorophthalanilic acids can be prepared best by the reaction of chloroform solutions of phthalic anhydride on the corresponding chloro-aniline. The o- and *m*- acids have not been previously recorded. The o-, m- and *p*-chlorophthalanils can be prepared by the fusion of the chloro-aniline with phthalic anhydride. The *ortho* and ***meta*** compounds have not been previously recorded.

SOUTH HADLEY, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. VII. THE ACTION OF POTASSIUM HYDROXIDE ON DIHYDROXY ACETONE

BY WILLIAM LLOYD EVANS AND WILLIAM ROBERT CORNTHWAITE

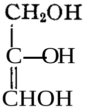
RECEIVED SEPTEMBER 22, 1927 PUBLISHED FEBRUARY 4, 1928

The studies of Hass and one of us[1] on the behavior of crystalline glyceric aldehyde in potassium hydroxide solutions, in which the concentration of the base varied from 0.2 to 6 N at 25 and 50°, showed that the amounts of the products obtained under the variable conditions employed were dependent on both the temperature and the normality of the alkali used. Pyruvic aldehyde, lactic, acetic and formic acids were the reaction products studied in the work on glyceric aldehyde. It was pointed out[2] that solutions of glyceric aldehyde[3] in the presence of potassium hydroxide should form an equilibrated system in the same manner as that which Lobry de Bruyn and Alberda van Ekenstein found existed in alkaline solutions of d-glucose and d-galactose. Furthermore, the active component of such a solution should be an enediol or its dissociation products similar to the systems postulated by Nef and his collaborators in the case of certain hexoses.

If these views are correct then it is clear that the following reaction represents the equilibrated condition existing between the three carbon atom compounds in an alkaline solution of glyceric aldehyde.

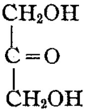
$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CHO \end{array}$$

Glyceric aldehyde



$$\begin{array}{l} CH_2OH \\ | \\ C{-}OH \\ \| \\ CHOH \end{array}$$

Triose enediol



$$\begin{array}{l} CH_2OH \\ | \\ C{=}O \\ | \\ CH_2OH \end{array}$$

Dihydroxy acetone

On the basis of this discussion it is expected that dihydroxy acetone should react in aqueous solutions of potassium hydroxide in the same general manner that glyceric aldehyde does. To determine this point was one of the principal objects of these experiments by reason of the importance of dihydroxy acetone in carbohydrate chemistry, especially in its structural relation to fructose.

Experimental Part

Reagents.—The potassium hydroxide, alcohol, phenylhydrazine, zinc carbonate, phosphoric and hydrochloric acids were of the same degree of purity as those used in the work on glyceric aldehyde. The dihydroxy acetone was purchased under the name of "Oxantin." Before using, it was kept in a vacuum desiccator over soda lime and calcium chloride for at least one week. It melted at 78–79° (corr.).[4]

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[1] Evans and Hass, THIS JOURNAL, 48,2703 (1926).

[2] Ref. 1, p. 2709.

[3] Wohl and Neuberg, Ber., 33,3110 (1900).

[4] Bertrand, *Ann. chim.*, [8] 3,255 (1904); Piloty, *Ber.*, 30, 3165 (1898).

Procedure.—In order that our data might be comparable with those obtained from the action of aqueous solutions of potassium hydroxide on glyceric aldehyde, every experimental detail of the work recorded in this report was an exact duplicate of that employed in the study of glyceric aldehyde, save that dihydroxy acetone was used instead of the aldehyde.

Products of the Reaction.—At various stages qualitative examination of our reaction mixtures was made for pyruvic aldehyde, acetol, lactic, acetic and formic acids.

Data.—Our quantitative data are shown in Figs. 1, 2, 3, 4, 5 and 6. For the sake of comparison the data by Evans and Hass from glyceric aldehyde are shown in the drawings by means of dotted lines.

Theoretical Part

The results obtained in these experiments were found to be in complete qualitative agreement with those obtained by the action of aqueous solutions of potassium hydroxide on glyeeric aldehyde. The suggestions offered for the reaction mechanism involved in the formation of pyruvic aldehyde, lactic, acetic and formic acids from glyceric aldehyde"are in accord with the data obtained by us in these experiments with dihydroxy acetone under precisely similar conditions. In addition to the discussion previously given concerning the general reaction involved in the formation of the above compounds, we wish to supplement it with the following brief statements with reference to our own data.

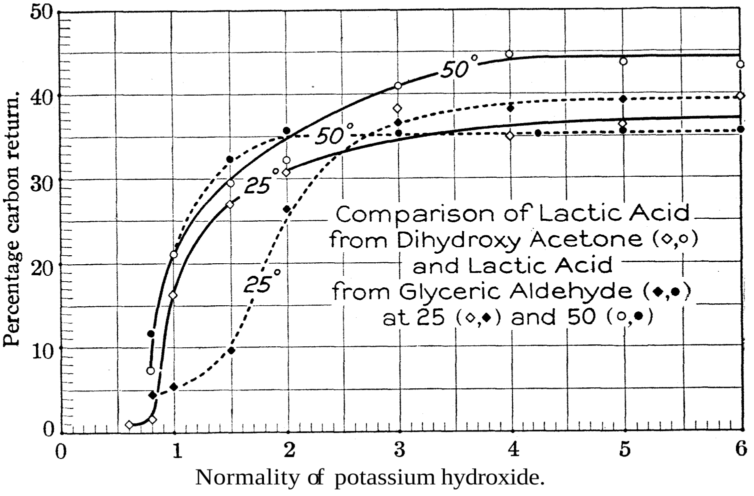

Fig. 1.

Lactic Acid.—If dihydroxy acetone and glyceric aldehyde form one and the same triose enediol, then it follows that lactic acid may be formed according to the following series of steps:[5]

Dihydroxy acetone ↘
or ⇄ Triose enediol ⟶ Pyruvic aldehyde ⟶ Lactic acid
Glyceric aldehyde ↗

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[5] Ref. 1, p. 2710; compare Neuberg, *Biochem.* Z., 71,250 (1915).

The molecular mechanism of this series of changes may be regarded as an application of the suggestion offered by Miss Marjorie Pickard Benoy and one of us[6] for the formation of saccharinic acid lactones from the enediols of glucose and galactose. The comparative yields of lactic acid from the two trioses are shown in Fig. 1. No lactic acid (zinc lactate) was found at 25° in potassium hydroxide solutions at either 0.2 or 0.4 N, but appreciable amounts were present at 0.6 *N*. It is clear from the graph of our data that our quantitative results are also in general agreement with the assumption that the lactic acid formation from glyceric aldehyde and dihydroxy acetone is following the same course.

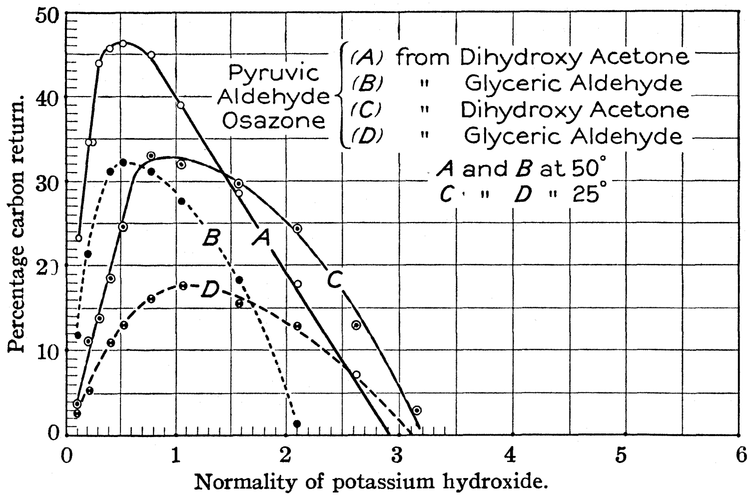

Fig. 2.

Pyruvic Aldehyde.—The percentage of dihydroxy acetone carbon obtained as pyruvic aldehyde is shown in Fig. 2. The data obtained from glyceric aldehyde are also given with certain correction factors applied which were previously omitted.[7] An examination of these curves shows in a very clear way the effect of temperature on the reaction by reason of the fact that the maximum yield of pyruvic aldehyde from both of these trioses occurs at a lower normality at 50° in each case than it does at 25°. Furthermore, it should be noted that the maximum yield of pyruvic aldehyde osazone from both compounds occurs at approximately the same normality for a given temperature. The fact that the maximum production of pyruvic aldehyde in dihydroxy acetone and glyceric aldehyde solutions occurs at practically the same alkali normality and that the general effect of temperature is also the same in each case, point very strongly to the assumption made above that a common intermediate

[6] Evans, Edgar and Hoff, This journal, 48, 2675 (1926).

[7] *See* Ref. 1, p. 2710.

compound, namely, the triose enediol, is formed in each case. Furthermore, the differences obtained in the yields of pyruvic aldehyde osazone from these two trioses at any given alkalinity under these experimental conditions seem to indicate that a condition exists in alkaline solution of these two carbohydrates similar to that observed by de Bruyn and van Ekenstein in alkaline solutions of glucose, mannose and fructose, that is, an equilibrated system in which the ratio of the amounts of the components present varied with the hexose used. It has been shown in this Laboratory[8] that the oxalic acid–carbon dioxide ratio obtained in the oxidation of these three well-known hexoses in strongly alkaline solutions of potassium permanganate tends toward the same value as the temperature and normality of the alkali are increased.

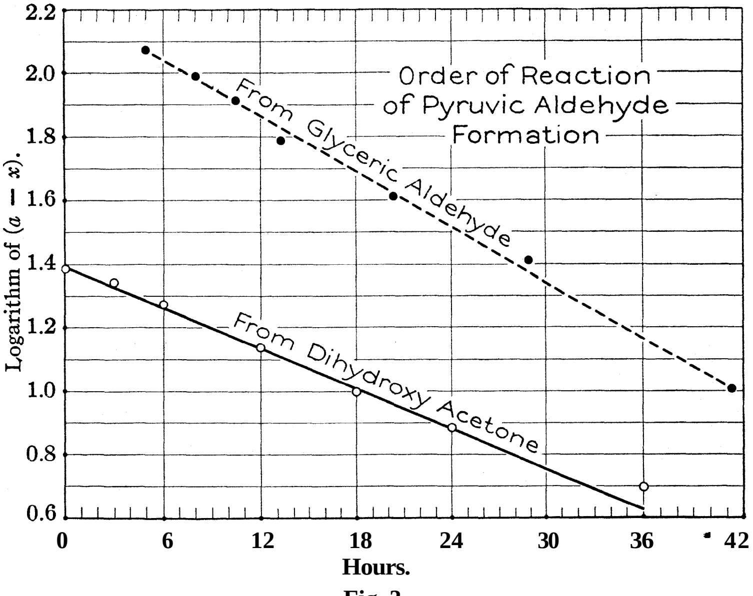

Fig. 3.

If alkaline solutions of glyceric aldehyde and dihydroxy acetone form a common triose enediol as an intermediate in the formation of pyruvic aldehyde osazone, and if the amounts of the components in the solutions varied according to the triose used, then the order of the reaction in the formation of the aldehyde from both compounds at a given alkalinity should be the same and the rate of the reaction should be different in each case. In Fig. 3 this is shown to be the case, that is, the reaction is monomolecular. The temperature used was 25°. The bearing of the recent experiments of Fischer, Taube and Baer[9] on the interpretation

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[8] Evans, Buehler, Looker, Crawford and Holl, This Journal, 47, 3085 (1925).

[9] Fischer, Taube and Baer, Ber., 60B, 479485 (1927).

of our experimental data is very important. These investigators have shown that crystalline glyceric aldehyde may be converted into dihydroxy acetone in boiling pyridine to the extent of 49%.[3]

In the work on glyceric aldehyde the view was expressed that acetic and formic acids resulted from a dissociation of pyruvic aldehyde into acetaldehyde and carbon monoxide. These two acids increase in amount with the alkalinity until a maximum has been reached, after which their amounts diminish due to the fact that the pyruvic aldehyde at that point is now being converted into lactic acid at a speed which increases with the alkalinity. This inter-relation of the formation of lactic, acetic and formic acids to the pyruvic aldehyde involved in the reaction of an aqueous solution of potassium hydroxide on dihydroxy acetone is clearly seen in Fig. 4. According to our experimental methods of measurement, the

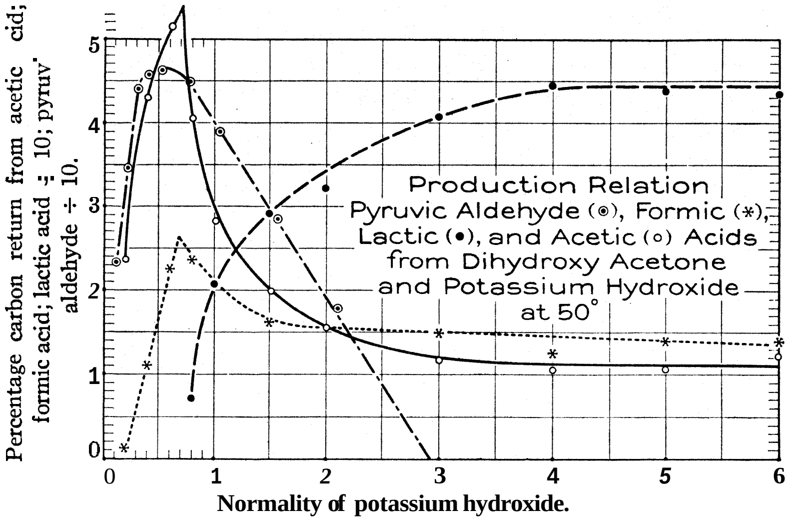

Fig. 4.

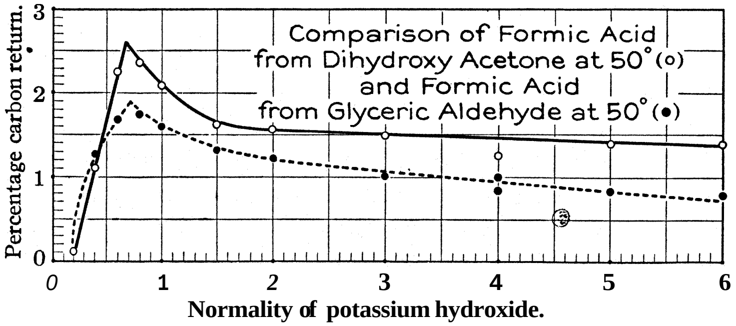

Fig. 5.

maximum yield for pyruvic aldehyde, acetic and formic acids and the minimum yield for lactic acid occur at approximately the same point of alkalinity. The maximum yield of dihydroxy acetone carbon as pyruvic aldehyde is approximately the same as the maximum for that of lactic acid. The formic and acetic acid yields are given in Figs. 5 and 6, respectively. The differences in the yields of these two acids from the two sources are not very great. It is also conceivable that the triose enediol of these reactions may undergo dissociation into the active forms of glycolic and formaldehydes, which in turn may react to yield other substances, among which would be formic acid. Our reaction mixtures were not examined for either glycol or glycolic acid. The view that a 1,2-enediol may undergo such a dissociation with subsequent chemical change has received much support in the recent experiments of Gustus and Lewis[10] on the action of alkaline hydrogen peroxide solution on 2,3,4,6-tetramethyl-d-glucose.

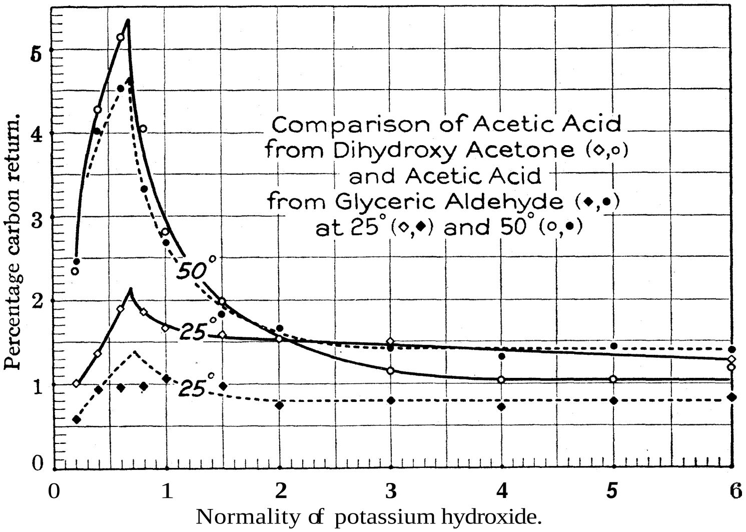

Fig. 6.

Summary

1. Molar solutions of dihydroxy acetone were treated with various concentrations of potassium hydroxide from 0.2–6 N at 25 and 50°. The resulting acetic, formic and lactic acids were measured quantitatively (Figs. 1, 5 and 6).

2. The yields of formic and acetic acids at 50° increased with the increasing alkali concentration until a maximum point was reached,

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[10] Gustus and Lewis, THIS JOURNAL, 49, 1512 (1927); see also Baly, *The Rice Institute Pamphlet, 12,* 93 (1925).

after which they diminished. The same effect was observed for acetic acid at 25°.

3. Molar solutions of dihydroxy acetone were treated with alcoholic phenylhydrazine solutions in the presence of various concentrations of alkali. The yield of pyruvic aldehyde osazone increased with the alkalinity to a maximum at both 25 and 50°, after which it diminished. Increasing temperature increased the yield of the osazone (Fig. 2).

4. The maximum yield of pyruvic aldehyde osazone from both trioses occurs at the same alkali normality for a given temperature. This maximum is attained at a lower alkali normality at 50° than at 25°.

5. The yields of lactic acid at 25 and 50° increased to a constant maximum with both the increasing alkalinity and temperature. The maximum point is practically the same as that for the pyruvic aldehyde at these temperatures.

6. The data obtained are shown graphically in comparison with a similar study on glyceric aldehyde. The results seem to indicate that both dihydroxy acetone and glyceric aldehyde in alkaline solutions form systems similar to those observed by de Bruyn and van Ekenstein in alkaline solutions of the hexoses.

7. The differences observed in the yields of pyruvic aldehyde osazone are thought to be due to the differences in the equilibrium existing between glyceric aldehyde, dihydroxy acetone and triose enediol in alkaline solutions. This point of view is supported by the fact that the order of the reaction is the same in both cases, while the rate of the reaction is different (Fig. 3).

8. Since both trioses are thought to form one and the same enediol, then the lactic acid must be derived from the pyruvic aldehyde arising from this common enediol. The acetic and formic acids are thought to be derived from a dissociation of pyruvic aldehyde into acetaldehyde and carbon monoxide. The minimum point for lactic acid yields is therefore related to the maximum yields for pyruvic aldehyde, acetic and formic acids. This inter-relation is shown in Fig. 4.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

CATALYTIC OXIDATIONS IN AQUEOUS SOLUTIONS. II. THE OXIDATION OF PRIMARY ALCOHOLS

BY NICHOLAS A. MILAS[1]

RECEIVED SEPTEMBER 24, 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

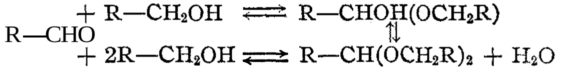
In a recent paper[2] of this series the author has shown that metallic oxides such as osmium tetroxide and vanadium pentoxide can be used, in aqueous solutions, to induce the oxidation of furfural and pyromucic acid by means of chlorates. The present paper describes several additional experiments in which vanadium pentoxide has been used to induce the oxidation of six of the primary alcohols.

The oxidation of alcohols has been the subject of a vast number of investigations which have occupied a period of more than a century. It is well established, therefore, that when primary alcohols are oxidized under ordinary conditions, the principal products which result from the oxidation are either aldehydes, or acids, or both. However, certain controlled oxidations of ethyl,[3] *n*-butyl,[4] isobutyl[5] and *iso*-amyl[6] alcohols yield esters as the principal products when the alcohols are present in excess. But such methods of oxidation are not applicable to all alcohols and any attempt to explain the formation of esters in these oxidations might lead to erroneous conclusions.

In the present paper a new catalytic method is described whereby the primary alcohols are simultaneously oxidized and esterified. It consists in the treatment of the alcohols, under proper care, with chlorates in dilute acid solution and in the presence of vanadium pentoxide as the catalyst.

Notwithstanding the great number of investigations published during the past hundred years on the oxidation of alcohols, comparatively little attention has been paid to the mechanism of the oxidation and subsequent esterification of these alcohols when the two reactions are taking place simultaneously in the same medium. Such a mechanism may be briefly postulated by the following equations

$$R—CH_2OH \xrightarrow{O} R—CHO + H_2O \qquad (1)$$



$$R—CHO \begin{cases} + R—CH_2OH \rightleftharpoons R—CHOH(OCH_2R) \\ \qquad\qquad\qquad\qquad\qquad \updownarrow \\ + 2R—CH_2OH \rightleftharpoons R—CH(OCH_2R)_2 + H_2O \end{cases} \qquad (2)$$

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[1] National Research Fellow in Chemistry.

[2] Milas, THIS JOURNAL, 49, 2005 (1927).

[3] Godefroy, "Thèse de la Faculté des Sciences de Paris," 1886, p. 43.

[4] Pierre and Puchot, *Ann.*, 163, 283 (1872); *Ann. chim. phys.*, [4] 28, 366 (1873).

[5] Robertson, "Organic Syntheses," John Wiley and Sons, Inc., New York 5, 23 (1925).

[6] Balbiano, *Gazz. chim. ital.*, 6, 238 (1876).

$$R{-}CHOH(OCH_2R) \xrightarrow{O} R{-}CO(OCH_2R) + H_2O \qquad (3)$$

It is quite obvious that the primary addition products of aldehydes when alcohols are present in excess would be unstable alcoholates or "hemiacetals," which may be regarded as secondary alcohols and therefore should be easily oxidized to the corresponding carbonyl derivatives before they are hydrolyzed. Although this assumption is purely hypothetical, at present, its justification is supported by the fact that, in the experiments to be described later, ester formation precedes acid formation. The organic acids formed during the reaction seem to result from the slow hydrolysis of the esters under the influence of the mineral acids. Furthermore, experiments in which acetaldehyde was used with the catalytic mixture failed to show an appreciable oxidation to acetic acid. However, when mixtures of equimolecular proportions of acetaldehyde and ethyl alcohol or acetaldehyde and n-butyl alcohol were used, instead of the aldehyde alone, ethyl and n-butyl acetates were formed, respectively.

In addition to hemiacetals, acetals might be formed as intermediate products of the oxidation of alcohols. Quite recently Adkins and his students[7] have carried out a series of experiments in which they found that the formation of acetals from mixtures of alcohols and aldehydes was markedly accelerated by certain salts and acids while the yields of acetals were greatly diminished with increased dilution. The latter observation of Adkins was more recently substantiated by Skrabal and Mirtl[8] who found that mineral acids act as catalysts in acetal hydrolysis which increases proportionately with increased dilution, while Skrabal, Brunner and Airoldi[9] assumed that such an hydrolysis takes place in steps hemiacetals being first formed. If this be the case, the acetals formed, during the oxidation of alcohols are immediately hydrolyzed under the influence of the mineral acids to hemiacetals which are then oxidized to the corresponding carbonyl derivatives. To confirm this view acetal, instead of ethyl alcohol, was used with the catalytic mixture. Ethyl acetate was the principal product of the oxidation.

Experimental Part

General Method.—The alcohols are oxidized very slowly, even at the boiling point of water, by a neutral aqueous mixture of sodium chlorate and vanadium pentoxide. However, in the presence of dilute sulfuric acid, the oxidation proceeds somewhat rapidly at first and slowly toward the end of the reaction. The appearance of a blue color, due to the reduction

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[7] (a) Adkins and Nissen, THIS JOURNAL, 44, 2749 (1922); (b) Adams and Adkins, *ibid.*, 47, 1358 (1925).

[8] Skrabal and Mirtl, *Z. physik. Chem.*, 111, 108 (1924).

[9] Skrabal, Brunner and Airoldi, ibid., 111, 118 (1924).

of vanadium pentoxide to vanadium trioxide,[2] is a proof of the absence of chlorates and consequently of the end of the reaction.

After several preliminary experiments the following general method, which is applicable to alcohols higher than methyl alcohol, was adopted. Solutions of 5% sulfuric acid containing the calculated amount of sodium chlorate and 5–10% in excess necessary to oxidize half of the alcohol present completely to the corresponding acid were mixed with small amounts of vanadium pentoxide and the alcohol in question, in a suitable container provided with a reflux condenser and a dropping funnel, and the mixture was heated slowly to 75–80°. A rise of temperature above 80° at this stage of the reaction should be avoided since it causes a rapid evolution of chlorine dioxide, which forms an explosive mixture with the alcohols. During the progress of the reaction some of the sulfuric acid is used up and should be replaced by adding the calculated amount of 6 N sulfuric acid, assuming that all of the original acid is consumed after a heating of five hours. In some cases it was found necessary to make even a second addition of the acid. After the final addition, the temperature was raised to the boiling point of the mixture and kept there till the end of the reaction.

Method of Analysis.—The esters were hydrolyzed by refluxing each for two hours with an excess of about 0.5 *N* alcoholic potash solution. The excess alkali was titrated with a solution of 0.2 N hydrochloric acid, using phenolphthalein. Therefore, the results are expressed in terms of 0.2 N potassium hydroxide solution. A blank was run with each analysis to check the strength of the alkali.

The yields of organic acids were estimated by titration according to Richardson and Bowen.[10] For the sake of comparison, a blank was run with the estimation of each organic acid. The yields of both esters and organic acids, as expressed below, represent the results of several experiments performed with each alcohol.

I. Oxidation of Methyl Alcohol with Sodium Chlorate and Vanadium Pentoxide

The general method described above is not applicable to the oxidation of methyl alcohol because of the explosive violence of the reaction between the formaldehyde formed and the chlorine dioxide liberated during the reaction. Therefore, the following modification of the method was finally adopted.

Seventy-three g. of sodium chlorate (Merck's U. S. P. grade) was dissolved in 130 cc. of 2.5% sulfuric acid and the mixture was slowly dropped by means of a dropping funnel at the rate of about 1 cc. per minute into a flask fitted with an efficient reflux condenser and containing 64 g. of methyl alcohol (Merck's "C. P." grade, free from acetone), 50 cc. of water and 0.3 g. of vanadium pentoxide.[11] The mixture was heated to 75–80°. At first the solution becomes orange-yellow and changes to blue at the end of the reaction. After ten hours of heating, 36 cc. of *6* N sulfuric acid was slowly dropped into the mixture and heating continued until the blue color appeared. This took thirty-six hours longer. During the progress of the reaction a large quantity of carbon dioxide was evolved. At the end of the reaction the mixture was found to contain traces of

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[10] Richardson and Bowen, J. *Soc.* Chem. *Ind.,* 25,836 (1906).

[11] For the preparation of this catalyst, see Milas, ref. **2,** p. 2007.

chloroform, as shown by the carbylamine test,[12] methyl formate, formic acid and small quantities of a condensation product the identity of which was not determined.

Isolation of Methyl Formate.—The reaction mixture from the above experiment was subjected to fractional distillation. The fraction boiling between 30 and 60° was collected, dried over anhydrous sodium carbonate and refractionated, the fraction distilling between 34 and 38° being collected and analyzed; yield, 5–6 g., or 8–10% of the alcohol taken.

Anal. Subs., 0.8372: required 68.8 cc. of 0.2 N KOH. Calcd. for $C_2H_4O_2$: 69.7 cc.

The aqueous solution was distilled once to free it from sulfuric acid and the blue color of vanadous oxide, which interferes with the end-point of the titration. The distillate was made up to a definite volume and lots of 50 cc. were titrated against 0.2 N sodium hydroxide (methyl orange, phenolphthalein). These indicated a yield of 8–9 g. of formic acid. No attempt was made to recover the unoxidized alcohol.

II. Oxidation of Ethyl Alcohol, Acetal and a Mixture of Equimolecular Proportions of Paraldehyde and Ethyl Alcohol with Sodium Chlorate and Vanadium Pentoxide

(*a*) Oxidation of Ethyl Alcohol.—Ninety-two g. of ethyl alcohol (abs.), 74 g. of sodium chlorate, 0.5 g. of the catalyst and 92 cc. of a 5% solution of sulfuric acid were brought together in a 500cc. Erlenmeyer flask provided with a reflux condenser and a dropping funnel. The mixture was heated very slowly to 75–80° and, after five hours of heating, 19 cc. of 6 N sulfuric acid was added very slowly and the temperature raised to the b. p. of the mixture. The blue color appeared after ten to twelve hours of heating. The mixture had separated into two layers, the upper of which was mostly ethyl acetate and some unconverted alcohol, while the lower contained alcohol, small quantities of acetaldehyde (forms a silver mirror in the cold with Tollens' reagent) and acetic acid. The entire mixture was subjected to fractional distillation; the fraction boiling between 70 and 90° was collected, dried over sodium carbonate, refractionated and the fraction distilling between 74 and 80° collected (74 g.) and analyzed by hydrolysis. This fraction proved to be 70–73% ethyl acetate, which is 60–61% of the total alcohol taken.

The entire aqueous solution, mixed with the fractions boiling above 80°, was distilled and the distillate made up to a definite volume. Samples of 50 cc. of this were titrated, indicating a total yield of 13.5–15.9 g. of acetic acid.

(b) Oxidation of Acetal.—One hundred g. of acetal (Kahlbaum's) was mixed with 62 g. of sodium chlorate, 0.3 g. of the catalyst and 100 cc. of 5% sulfuric acid and the mixture heated very slowly under a reflux condenser to 75–80°, this temperature being maintained till the end of the reaction, which took nine hours. The experiment yielded 45 g. of ethyl acetate, 36 g. of acetic acid and some alcohol which had presumably resulted from the hydrolysis of the ester.

(c) Oxidation of an Equimolecular Mixture of Paraldehyde and Ethyl Alcohol.—When acetaldehyde alone was treated with the oxidizing mixture in presence of 5% sulfuric acid, paraldehyde was chiefly formed, and when this mixture was further heated at 75–80° for thirty-four hours, no additional change was noticed. This mixture yielded only traces of acetic acid, as shown by the ferric chloride test.[13] However, when the aldehyde was mixed with equimolecular proportions of alcohol, oxidation occurred immediately, with ethyl acetate resulting as the main product of the reaction.

Fifty g. (1.14 moles) of paraldehyde (Kahlbaum's) was mixed with 52.3 g. (1.14 moles) of absolute alcohol, 50 g. of sodium chlorate, 0.3 g. of the catalyst and 100 cc. of

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[12] Hofmann, *Ann.*, 146, 107 (1868).

[13] Weston, "A Scheme for the Detection of the More Common Classes of Organic Compounds," Longmans, Green and Co., 1912, p. 27.

5% sulfuric acid and the mixture was heated very slowly, under a well-cooled reflux condenser, to 30°. In the beginning the temperature of the reaction mixture should not be allowed to rise above 40°, otherwise the reaction will become too violent and uncontrollable. After five hours the reaction has somewhat moderated and the temperature may now be raised to 75–80", and 19 cc. of 6 N sulfuric acid slowly added to the mixture and the heating continued for six additional hours before the blue color appears. The experiment yielded 54 g. of ethyl acetate and 21.3 g. of acetic acid. Small quantities of unconverted alcohol and aldehyde were also recovered.

During the above reactions the active form of the aldehyde is presumably the monomolecular, which is regenerated under the influence of sulfuric acid. This is well shown by the work of McLeod[14] on the polymers of acetaldehyde.

These results, while not absolutely conclusive, indicate the plausibility of the view presented in the early part of this paper.

III. Oxidation of n-Propyl Alcohol with Sodium Chlorate and Vanadium Pentoxide

Ninety g. of n-propyl alcohol (Kahlbaum's) was mixed with 58 g. of sodium chlorate, 0.5 g. of the catalyst and 90 cc. of 5% sulfuric acid and the mixture slowly heated to 75–80° until the violent reaction moderated; then the temperature was raised to boiling. After five hours of heating, the first portion of 18 cc. of 6 *N* sulfuric acid was added, the heating continued for ten hours longer when a second portion of 22 cc. of the acid was slowly added, and the heating again continued until the blue color appeared. Twenty to twenty-two hours were required for the completion of the reaction. The mixture was then cooled and the ester layer separated from the aqueous layer. The former consisted chiefly of propyl propionate, propyl alcohol, propionic acid, small quantities of propionaldehyde and a chlorinated ester. It was shaken several times with a 4% solution of sodium hydroxide to remove the acid and most of the alcohol, washed twice with water, dried over anhydrous sodium carbonate and fractionated. The fraction distilling between 121 and 124° (4245 g.) consisted of pure propyl propionate free from any chlorinated products. The ester yield was 48–51% of the total alcohol taken.

Anal. Subs., 1.2983: required 56.25 cc. of 0.2 N KOH. Calcd. for $C_6H_{12}O_2$: 55.96 cc.

A small quantity of the chlorinated ester boiling between 140 and 150° with decomposition was isolated but not analyzed.

The washings from the ester layer were mixed with the aqueous layer, treated with dilute sulfuric acid in excess and distilled. The distillate was made up to a liter, and a portion of it was exactly neutralized and evaporated to dryness on the water-bath. The dry salt, treated with absolute alcohol and a few drops of concd. sulfuric acid, gave a decided odor of ethyl propionate. Fifty-cc. samples of the distillate were then titrated and the total yield of propionic acid estimated. These indicated a total yield of 22–24 g. of propionic acid.

IV. Oxidation of n-Butyl Alcohol with Sodium Chlorate and Vanadium Pentoxide[15]

Eighty-nine g. of n-butyl alcohol (b. p. 116.5–118°) was mixed with 48 g. of sodium chlorate, 0.5 g. of the catalyst and 90 cc. of 5% sulfuric acid and the mixture heated

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[14] McLeod, Am. Chem. Jour., 37, 27 (1907).

[15] I am indebted to William L. Ruigh of this Laboratory for the preliminary experiments on this alcohol.

slowly, under a reflux condenser, to 75–80° for two hours, then to the b. p. for three hours longer, when **18** cc. of **6** N sulfuric acid was slowly added and the heating continued for five hours longer. A second portion of **22** cc. of the acid was then added and the heating continued till the blue color appeared. Fifteen to eighteen hours were required for the completion of the reaction. The mixture was then cooled and the layers separated. The ester layer was washed several times with a **4%** solution of sodium hydroxide, twice with water, dried over sodium carbonate and fractionated. After two fractionations the fraction distilling between **164** and 166° **(4143** g.) was collected and analyzed; yield, 47–49% of the total alcohol taken.

Anal. Subs., **1.0892:** required **38.22** cc. of **0.2** N **KOH.** Calcd. for $C_8H_{16}O_2$: **37.85** cc.

Besides the ester, small quantities of chlorinated products boiling with decomposition from 10–15° higher than the ester were isolated but not analyzed. From **20–25** g. of unoxidized alcohol was recovered. Small quantities of butylaldehyde were also isolated.

The washings from the ester layer were combined with the aqueous layer, treated with sulfuric acid and distilled, and the distillate was made up to a liter. A portion of this was exactly neutralized, and evaporated to dryness. The salt, treated with calcium chloride in the hot, formed a white precipitate which persisted only in cloudy form when the mixture was cooled. The odor of the free acid was characteristic of that of butyric acid. Fifty-cc. samples of the distillate were then titrated and indicated a yield of 5–6.5 g. of n-butyric acid.

V. Oxidation of *iso*Butyl Alcohol with Sodium Chlorate and Vanadium Pentoxide

Eighty-nine g. of isobutyl alcohol (Kahlbaum's) was mixed with **48** g. of sodium chlorate, **0.5** g. of the catalyst and **90** cc. of 5% sulfuric acid. The mixture was treated in exactly the same manner as in the case of normal butyl alcohol except that the number of hours to complete the reaction was only 15–16. The ester layer was also treated similarly, fractionated twice, and the fraction distilling between **147** and 150° (40–42 g.) collected and analyzed; yield, **46–48%** of the alcohol taken.

Anal. Subs., **1.0282:** required **36.15** cc. of **0.2** N **KOH.** Calcd. for $C_8H_{16}O_2$: **35.71** cc.

During the above oxidation large quantities of carbon dioxide were evolved, and some of the alcohol was oxidized to acetone, considerable quantities of which were detected by the iodoform reaction. Isobutylaldehyde and small quantities of chlorinated products were also isolated.

Isobutyric acid was identified by preparing its sodium salt, which was found to decolorize instantly dilute potassium permanganate. Acetone was identified as one of the oxidation products. Neither the salt nor the free acid formed a precipitate with calcium chloride either in the hot or in the cold. The total yield of isobutyric acid, as determined by titration, was 4–5 g.

VI. Oxidation of *iso*-Amyl Alcohol with Sodium Chlorate and Vanadium Pentoxide

Seventy-five g. of iso-amyl alcohol (Kahlbaum's pyridine free) was mixed with **40** g. of sodium chlorate, 0.5 g. of the catalyst and 150 cc. of a **5%** solution of sulfuric acid and the mixture heated slowly to 75–80° for one hour; then the temperature was raised to boiling. After four hours **36** cc. of **6** N sulfuric acid was added and the heating continued for eight hours longer before the blue color appeared. The ester layer was shaken several times with a 4% solution of sodium hydroxide, washed twice with water, dried over sodium carbonate and fractionated. After three fractionations the fraction distilling between 190 and 195" (33–35 g.) was collected and analyzed; yield of iso-amyl *iso*-valerate, 45–48% of the alcohol taken.

Anal. Subs., 2.0247: required 59.40 cc. of 0.2 *N* KOH. Calcd. for $C_{10}H_{20}O_2$: 58.85 cc.

Besides iso-amyl isovalerate, isovaleric aldehyde, some unoxidized alcohol, small quantities of chlorinated products, acetone and carbon dioxide were identified.

When the washings from the ester layer were mixed with the aqueous layer and the mixture was treated with sulfuric acid, a layer of isovaleric acid separated out. The mixture was extracted with 300 cc. of ether and the ether extract dried over anhydrous sodium sulfate and subjected to fractionation. Most of the high-boiling liquid distilled between 175 and 177°. This was almost pure isovaleric acid; yield, 12–13 g. The acid had a very rancid odor and gave a gelatinous precipitate with a solution of zinc sulfate.

Summary

1. Vanadium pentoxide, in dilute sulfuric acid solution, induces the oxidation of methyl, ethyl, *n*-propyl, n-butyl, isobutyl and iso-amyl alcohols, acetal and mixtures of equimolecular proportions of paraldehyde and ethyl alcohol and paraldehyde and n-butyl alcohol with chlorates to give esters as the principal products.
2. Organic acids, small quantities of aldehydes and chlorinated products, acetone and carbon dioxide were isolated as by-products in the oxidation of some of the alcohols.
3. A tentative mechanism of the oxidation is presented.

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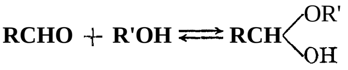
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

HEMIACETAL FORMATION AND THE REFRACTIVE INDICES AND DENSITIES OF MIXTURES OF CERTAIN ALCOHOLS AND ALDEHYDES

BY HOMER ADKINS AND A. E. BRODERICK

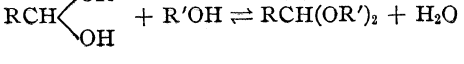
RECEIVED OCTOBER 10, 1927 PUBLISHED FEBRUARY 4, 1928

Heat is evolved when certain alcohols and aldehydes are mixed with each other. The addition of a catalyst such as hydrogen chloride or calcium chloride to the solution results in acetal formation. Presumably the pure alcohol and aldehyde react by addition according to the equation



$$RCHO + R'OH \rightleftharpoons RCH\begin{cases}OR' \\ OH\end{cases}$$

The hemiacetal in the presence of a catalyst may then react with alcohol to form an acetal and water



$$RCH\begin{cases}OR' \\ OH\end{cases} + R'OH \rightleftharpoons RCH(OR')_2 + H_2O$$

Our investigations of the reactivities of alcohols and aldehydes in acetal formation have led us to seek more precise evidence as to the justifiability of this hypothesis. We have therefore measured the refractive indices and the densities of mixtures of certain alcohols and aldehydes. A summary of the results is presented in the table.

TABLE I

REFRACTIVE INDICES OF MIXTURES OF VARIOUS ALCOHOLS AND ALDEHYDES[a]

Acetaldehyde and ethanol		Acetaldehyde and isopropanol		Heptaldehyde and *iso*propanol		Heptaldehyde and ethanol	
%	R. i.	%	R. i.	%	R. i.	%	R. i.
0	1.36424	0	1.38516	0	1.36994	0	1.35828
11.9	1.37134	13.3	1.38391	11.7	1.38113	11.3	1.36708
33.1	1.38266	33.6	1.38247	17.2	1.38381	20.5	1.37452
40.2	1.38583	42.6	1.38008	20.0	1.37640	30.8	1.38266
55.1	1.38506	52.6	1.37640	40.0	1.39318	40.4	1.38979
56.3	1.38612	64.4	1.37218	50.4	1.39699	51.2	1.39768
68.1	1.37762	70.6	1.36864	62.6	1.39945	61.1	1.40419
84.1	1.36424	74.2	1.36552	69.8	1.40350	71.1	1.40855
75.5	1.37480	81.0	1.36044	80.6	1.40577	81.0	1.41113
90.8	1.35686	92.1	1.35193	89.4	1.40765	90.1	1.41103
95.7	1.35097	95.8	1.34941	91.9	1.40835	95.5	1.41028
100	1.34445	100	1.34445	100	1.40884	100	1.40884

Butyraldehyde and *tert.*-butanol		Anisaldehyde and ethanol		Benzaldehyde and ethanol		
%	R. i.	%	R. i.	%	R. i.	d^{25}_4
0	1.38458	0	1.35828	0	1.35828	0.7839
4.8	1.38360	12.5	1.38008	7.8	1.37050	.8020
13.1	1.38333	23.5	1.39876	16.7	1.38448	.8251
21.3	1.38237	34.1	1.41782	36.3	1.41702	.8728
30.9	1.38094	45.3	1.44012	46.7	1.43770	.8933
41.1	1.38018	54.5	1.45956	56.5	1.45567	.9225
51.1	1.37932	61.9	1.47518	62.7	1.46562	.9391
66.9	1.39837	77.0	1.51040	67.3	1.47429	.9499
79.9	1.37772	84.7	1.52992	84.0	1.50774	.9935
81.6	1.37861	92.2	1.54966	83.9	1.52387	1.0155
92.5	1.37743	95.4	1.55733	96.1	1.53423	1.0300
100	1.37875	100	1.57004	100	1.54254	1.0403

[a] The readings of refractive indices are believed to be reproducible to within less than 0.0001. The concentration of the aldehyde was accurate to within less than 1% for all mixtures except those having a high content of acetaldehyde, for which an accuracy of less than 2% is claimed.

The percentages given in the table represent the per cent. by weight of aldehyde contained in the aldehyde-alcohol mixture. All measurements were made at 25° except for those mixtures containing acetaldehyde, which were made at 8°. The densities $(d^{25°}_4)$ for the benzaldehyde-ethanol mixtures are also given in the table. The results of a few significant determinations on mixtures other than the seven noted in the table are as follows.

74.4% Anisaldehyde, 25.6% ethanol: d_4^{25}, 1.0135; n_D^{25}, 1.50432.
60.7% Butyraldehyde, 39.3% ethanol: d_4^{25}, 0.8442; n_D^{25}, 1.39134.
100% Anisaldehyde: d_4^{25}, 1.1192; n_D^{25}, 1.57031.
50% Acetaldehyde, 50% *tert.*-butyl alcohol: n_D^8, 1.37470.
100% *tert.*-butyl alcohol: n_D^8, 1.38684.

The refractive indices were determined by means of a Pulfrich refractometer. The densities were determined by the use of a pycnometer. The alcohols and the acetaldehyde were purified as described elsewhere;[1] ethanol, b. p. 77.8–78.0°; *iso*propyl alcohol, b. p. 82.1–82.5°; *tert.*-butyl alcohol, b. p. 82.5–82.7°, m. p. 25°. The bisulfite derivative of butyraldehyde was made from the liquid products of the air oxidation of butanol over copper. The aldehyde was liberated from the bisulfite compound by sodium carbonate and steam distilled. The aqueous mixture was repeatedly dried over calcium chloride and then fractionated. The portion boiling between 73 and 74° was collected and used within two or three days. All samples of butyraldehyde recovered from the commercial product or allowed to stand for a time in the laboratory boiled 6 or 7° too high. The benzaldehyde was fractionated and had a boiling point of 168.4" and $d_4^{20°}$, 1.04885. The heptaldehyde was fractionated from the product of the Eastman Kodak Company; b. p. 175.0–175.5°. The anisaldehyde was similarly obtained and distilled at 130–131° at 15 mm. No cinnamic aldehyde could be obtained sufficiently colorless so that it could be used in this work, although the compound is usually so described.

The refractive indices of mixtures of ethanol and acetaldehyde, ethanol and heptaldehyde and isopropanol and acetaldehyde have been plotted in Fig. 1. The curved lines pass through the experimentally determined points, while the straight lines represent what would be the refractive indices if the alcohol and aldehyde did not react. It is obvious that reaction has taken place between the alcohols and aldehydes. The curve for heptaldehyde and isopropanol is similar to that for *iso*propanol and acetaldehyde, although the divergence of the curve from the straight line is not so great. The single mixture of butyraldehyde and ethanol whose constants were measured shows a divergence similar to that of acetaldehyde and ethanol.

The refractive indices of mixtures of benzaldehyde and ethanol, anisaldehyde and ethanol and of tertiary butanol and butyraldehyde are quite different from what they would be if the alcohol and aldehyde did not react with each other. However, in the case of these pairs the experimental curve is below the straight line rather than above it, as is the case with the data shown in Fig. 1.

The refractive index is, of course, a function of the density of the liquid as well as of the constitution of the compound or compounds which com-

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[1] Adkins and Broderick, This Journal, 50, 178 (1928).

pose the liquid. The densities of all of the benzaldehyde-ethanol mixtures, of a single mixture of butyraldehyde-ethanol and of an anisaldehyde-ethanol mixture have been determined. These data have a relationship to the densities of the corresponding alcohols and aldehydes similar to that found to exist between the index of refraction of the mixtures and of the corresponding alcohol and aldehyde. However, the change in refractive index is not due solely to the change in density. This is evidenced by the fact that if one calculates the refractive index of a mixture of 74.4% anisaldehyde and 25.6% ethanol upon the assumption that these compounds are present as such, but that the mixture has the observed density of 1.0333, the value 1.51605 is obtained. The experimental value for this mixture is 1.50432, indicating that a constitutional change has taken place. However, in the case of butyraldehyde and ethanol, the change in refractive index parallels the density change. The molecular refraction based upon the observed indices of refraction of an equimolecular mixture of the alcohol and aldehyde was 33.24. The value calculated upon the assumption that the alcohol and aldehyde are present but have the observed density (0.8044) is 33.22. The calculated value for the molecular refraction of the hemiacetal is 32.02, the value 2.501 being taken for each carbon, 1.051 for each hydrogen, 1.521 for the hydroxyl oxygen and 1.603 for the ether oxygen.

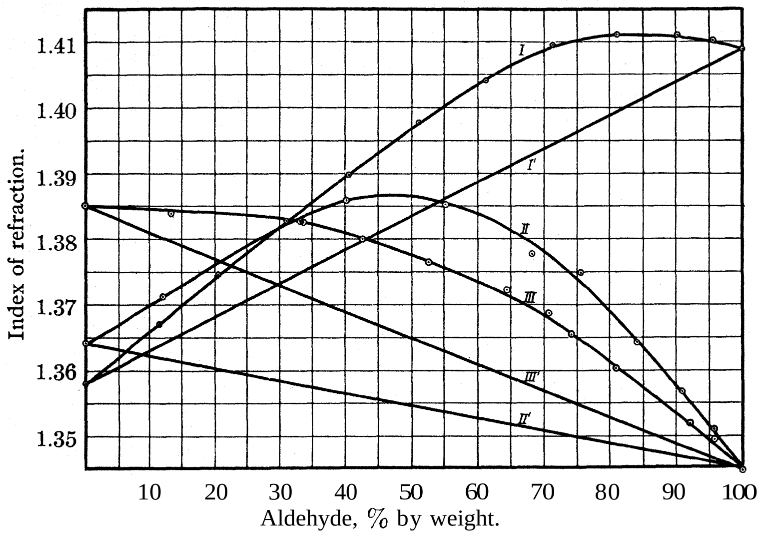

Fig. 1.—Refractive indices of mixtures of certain aldehydes and alcohols. The per cent. by weight of aldehyde in the mixture is plotted (abscissa) against the refractive index of the mixtures (ordinate). Curve I is for heptaldehyde and ethanol at 25°; Curve II, acetaldehyde and ethanol at 8°; Curve III, acetaldehyde and isopropanol at 8°. The straight lines show refractive indices of ideal solutions.

Success in detecting reaction between an alcohol and an aldehyde through determinations of the refractive indices of mixtures of the two is dependent upon whether or not the refractive index of the reaction product differs considerably from that of the ideal mixture. A small or even a total lack of difference of the constants from those of ideal mixtures does not prove that no reaction has taken place. It must also be kept in mind that two distinct questions may be asked with regard to the reaction under consideration. First, do certain aldehydes react with certain alcohols, and, second, how far to the right is the equilibrium point in those cases where reaction occurs? The first question is answered in the affirmative by the data for all nine of the pairs of compounds investigated. An answer to the second question can only be attempted in those cases where the observed values lie on a line having a pronounced curvature. This is true for only two or perhaps three of the seven complete sets of data, that is, for acetaldehyde-ethanol and heptaldehyde-ethanol and perhaps for acetaldehyde-isopropanol.

It should be emphasized that in a consideration of the experimental data from this point of view, the significant thing is not the point at which the refractive index is at a maximum but is the point at which there is the maximum *deviation* of the curve from the straight line representing the refractive indices of ideal solutions. For example the maximum deviation for heptaldehyde-*iso*propyl alcohol is for concentrations of between 60 and 70% heptaldehyde. These compounds are in molecular proportions when there is 65% heptaldehyde present. The maximum deviation for acetaldehyde-ethanol is for concentrations between 50 and 55% acetaldehyde. The equimolecular mixture contains 49% of acetaldehyde. The maximum deviation for acetaldehyde-isopropyl alcohol is almost constant over a wide range of concentrations from 35 to 60% aldehyde. The equimolecular mixture contains 42% of acetaldehyde. Thus it is seen that in the case of these three mixtures the maximum deviation of refractive indices from those of ideal solutions comes at approximately the concentration of reactants necessary for the formation of a hemiacetal, thus indicating that the equilibrium point of the reaction for these compounds is quite far to the hemiacetal side of the equation.

Summary

The refractive indices and densities of mixtures of several pairs of alcohols and aldehydes have been determined over the range from pure alcohol to pure aldehyde. All the data obtained indicate that chemical reactions took place and that, at least in some cases, one mole of alcohol and one mole of aldehyde reacted almost quantitatively to form what is presumably a hemiacetal.

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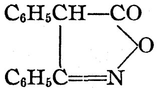
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

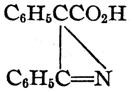
DIPHENYL ISOXAZOLONE
A STUDY OF THE TAUTOMERISM OF ISOXAZOLONES

BY E. P. KOHLER AND A. H. BLATT

RECEIVED OCTOBER 13, 1927 PUBLISHED FEBRUARY 4, 1928

Diphenyl isoxazolone was first described by Beckmann and Paul,[1] who in 1891 obtained it incidentally while studying the action of sodium on desoxybenzoin. Realizing that the substance must be an anhydride of the oxime of phenyl benzoyl acetic acid, they considered the two formulas

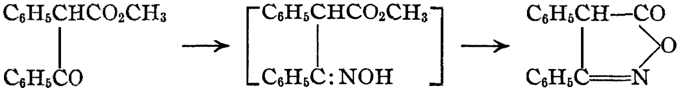




When they found that it could be titrated with a standard base of which it neutralized exactly one equivalent, they decided in favor of the second formula and named it "anhydro oximido benzoyl acetic acid."

Six years later Walther and Schickler[2] came across the substance again while examining the action of hydroxylamine on the amide of phenyl benzoyl acetic acid. They were unaware of the earlier work, made a faulty analysis of their product and, impressed by its acidity, formulated it as the oxime of phenyl benzoyl acetic acid.

Quite recently the same substance turned up again, this time as a product of the oxidation of 3,4-diphenyl-5-hydroxy-5-benzoyl isoxazoline with sodium peroxide.[3] It was then made synthetically by the most general reaction available for the preparation of isoxazolones:



The isoxazolone was described as a substance capable of existing in two modifications—the ordinary form first mentioned by Beckmann and Paul, and an unstable, lower-melting, more acidic form which immediately yielded a copper derivative when its ethereal solution was shaken with aqueous copper acetate. This conclusion led to the present investigation. If correct, it would mean that diphenyl isoxazolone is the only isoxazolone derivative—perhaps the only heterocyclic compound—of which desmotropic modifications can be isolated, and it would also mean that diphenyl isoxazolone would be the best material for the study of the structure of solid isoxazolones, and of their tautomerism in solution.

This conclusion now appears to us to be doubtful because we have been unable to prepare a sample of isoxazolone that does not immediately yield

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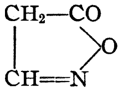
[1] Beckmann and Paul, Ann., 266, 20 (1891).

[2] Walther and Schickler, J. prakt. *Chem.*, [2]55, 316 (1897).

[3] Kohler, THIS JOURNAL, 46, 1741 (1924).

a copper derivative. The analytical sample (0.5 g.) left from the earlier work gave an ethereal solution which, when shaken with aqueous copper acetate, at first produced only a faint opalescence. Then, very gradually, apparently as a consequence of rearrangement, it deposited the deep blue copper derivative, complete deposition requiring several hours. Numerous attempts to prepare another sample showing this behavior were all unsuccessful; we are therefore unable to exclude the possibility that lower-melting preparations contain a small quantity of an impurity which does not materially change the composition.

Rut even though we failed to isolate desmotropic modifications we nevertheless secured reliable evidence on the structure of the isoxazolone, both as solid and in solutions. The various methods by which alkyl and aryl isoxazolones have been prepared leave no doubt as to the nature of the carbon chain or the position of the hydrocarbon residues; the only uncertainty is the location of one hydrogen atom. This is created by the fact that various isoxazolone derivatives correspond to three tautomeric forms of the parent substance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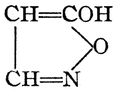
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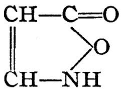
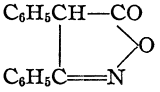
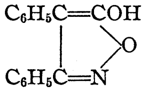
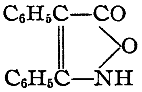

III

Most authors represent alkyl and aryl isoxazolones as derivatives of form I—largely, doubtless, because this form is most closely related to the substances from which these isoxazolones are usually obtained. Uhlenhuth,[4] who made the most extensive investigation of mono- and di-alkyl isoxazolones, adopted Formula III because he found that phenyl isoxazolone, when methylated by way of the silver salt, gave an N-methyl derivative—evidence that would not now be regarded as weighty. Formula III was also preferred by Moureu and Lazennec[5] because in their opinion it agrees best with all methods of preparation.

The corresponding formulas for the possible modifications of diphenyl isoxazolone are


IV


V


VI

In order to get a basis on which to distinguish between these formulas we have titrated solutions of the substance with bromine by the Kurt Meyer method, examined the behavior of the substance itself as well as that of its acyl and alkyl derivatives towards ozone, and determined both the

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[4] **Uhlenhuth, Ann., 296, 36** (1897).

[5] Moureu **and** Lazennec, *Bull. soc. chim.*, [4] **1**, 1092 (1907).

quantity of gas evolved and the amount of reagent consumed when the substance reacts with methyl magnesium iodide.

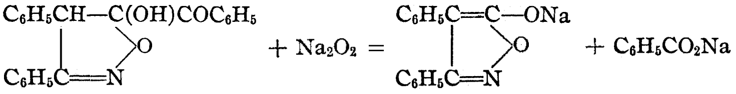
The bromine titrations show quite conclusively that solutions of diphenyl isoxazolone contain at least two forms. Unless prepared in a special manner, alcoholic solutions give bromine values which indicate 90% of "enolic" modifications. Since these solutions are strongly acidic, give color reaction with ferric chloride and copper derivatives with copper salts, this "enolic" modification must be the hydroxy isoxazol represented by V. In addition to this hydroxylic form the solution must contain 10% of one or both of the other modifications. In order to distinguish between these forms we subjected solutions of the isoxazolone to the action of ozone.

The forms represented by IV and V would not be expected to yield ozonides and neither of these forms would be likely to give definite products when oxidized with concentrated ozone, because the former contains no ethylenic linkage and the second is essentially aromatic. The modification represented by VI, on the other hand, would be expected to form an ozonide like every other phenylated ethylene derivative. Experiments showed that the isoxazolone is very slowly attacked by 6% ozone but neither forms an ozonide nor yields any of the normal decomposition products of ozonides. It can safely be concluded, therefore, that solutions of diphenyl isoxazolone contain a mixture of the "ketonic" modification IV and the "enolic" modification V; there is no evidence of the presence of form VI.

The bromine titrations also supply conclusive evidence that the solid isoxazolone is not the enolic modification. When these titrations were made as speedily as possible, with the purest materials that could be prepared, in apparatus that had been carefully steamed, they always gave values far below the usual 90% and in one case even below 50% of enol. The freshest solutions therefore contain the least enol, and since there is no evidence whatsoever of the presence of the imino form, even in the most concentrated solutions, it seems necessary to conclude that the solid substance is the "ketonic" modification V. The "keto-enol" system differs from most others only with respect to the rapidity with which it attains equilibrium.

II. Preparation

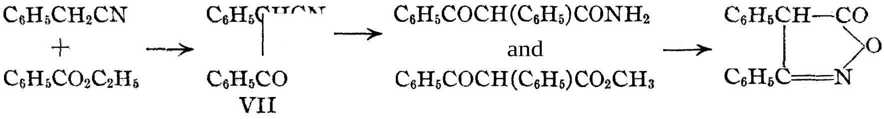
Of the various methods of formation enumerated in the introduction, two merit consideration as methods of preparation: the oxidation of hydroxy benzoyl diphenyl isoxazoline and the action of hydroxylamine on phenyl benzoyl acetic ester. The first is represented by the equation



This method gives an excellent yield but the hydroxy isoxazoline can be obtained only by a long series of reactions[6] starting with phenyl nitro methane. The preparation of this is in itself an arduous task. Our procedure for the oxidation was as follows.

To a solution of 70 g. of sodium peroxide in 810 g. of ice and 700 cc. of water is added, gradually, 35 g. of the hydroxy isoxazoline. This mixture is stirred for eight hours, then left overnight. The next day the sodium salt is collected on a filter and washed with dilute sodium carbonate, filtrate and washings being discarded. The sodium salt is dissolved in 600–800 cc. of water, the solution filtered, the clear filtrate acidified and left to itself until the precipitation is complete. The precipitate is thoroughly washed with water, dried and boiled with ether. This removes benzoic acid and small quantities of other impurities and leaves a crude product that melts at 150–155°; yield, 90%.

The successive steps in the second method of preparation are as follows:



Here the principal difficulty lies in the first step. By a modification of the procedure of Bodroux it was found possible to effect this condensation on a large scale and since, contrary to the observations of Walther and Schickler, the isoxazolone can be made from the amide as well as from the ester, this method of preparation proved to be the more convenient.

Phenyl Benzoyl Aceto Nitrile (VII).—After preliminary trials with the various agents that have been used for condensing ethyl benzoate with benzyl cyanide[7] we decided in favor of Bodroux's method but, possibly owing to the quality of our sodamide, our yield was only 35%. By changing the procedure and also the proportions of reactants this was increased to 60% which is still much lower than the 85% reported by Bodroux. Our procedure was as follows.

In a one-liter flask fitted with a dropping funnel, reflux condenser and motor stirrer, 40 g. of finely powdered sodamide is placed under 500 cc. of absolute ether. To this is added in the course of half an hour, during which the mixture is stirred constantly, 60 g. of benzyl cyanide. The mixture, which during the addition acquires a dark red color, is boiled for half an hour, then cooled in an ice-bath while 75 g. of ethyl benzoate is added. This requires about half an hour and is accompanied by the separation of a yellow solid. The mixture is then kept at room temperature for several hours.

The products from two or three such operations are combined and slowly poured into cold 50% alcohol. The resulting solution is diluted with water until it separates into two layers. The aqueous layer is thoroughly extracted with ether, then acidified with a mixture of ice and concentrated hydrochloric acid. This precipitates the nitrile as an oil which slowly solidifies. After washing with chilled methyl alcohol and drying,

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[6] Ref. 3, p. 1738.

[7] (a) Walther and Schickler, ref. 2, p. 308; (b) Ghosh, *J. Chem. Soc.*, 109, 116 (1916); (c) Bodroux, *Bull. soc. chim.*, [4] 9,651 (1911); (d) *ibid.*, p. 726. After we had prepared our material, Wislicenus, Eichert and Marquart, *Ann.*, 436, 92 (1925), described a preparation in which they used metallic potassium as a condensing agent. This gave a yield of 80%.

the yield of crude solid is 120–130 g. from 120 g. of benzyl cyanide, or 55–60%. The crude nitrile—m. p. 90–92°—is readily purified by crystallization from dry methyl alcohol, but this is unnecessary if it is to be used for making the isoxazolone.

For the purpose of converting the nitrile into diphenyl isoxazolone it was first esterified with methyl alcohol and hydrochloric acid, essentially as described in earlier papers. The result was a mixture of ester and amide in proportions that depended on the conditions. Each of these was turned into the isoxazolone. To this end a methyl alcoholic solution of the substance and 20% excess of hydroxylamine hydrochloride was boiled—for two hours in the case of the ester, four hours in the case of the amide. Most of the isoxazolone crystallized on cooling; the balance was precipitated by diluting the solution with water. Both ester and amide gave practically quantitative yields of a crude washed and dried product which melted and decomposed at 150°. For most purposes this was simply boiled with dry ether which removed small quantities of impurities and thereby raised the melting point to 155–157°. The purest product was obtained by careful recrystallization from benzene. This melted and decomposed sharply at 159°.

3,4-Diphenyl isoxazolone is readily soluble in methyl and ethyl alcohols, sparingly soluble in chloroform, carbon tetrachloride and benzene, almost insoluble in ether. Its resistance to hydrolytic agents is impressive; neither prolonged boiling with saturated methyl alcoholic potassium hydroxide nor protracted heating to 110–115° with concentrated hydrochloric acid produced any effect at all, and more than 85% of it was recovered after long boiling with a 60% solution of sulfuric acid in methyl alcohol. It likewise resists the action of hydroxylamine and phenyl hydrazine and a sample which had been boiled for five hours with zinc dust and glacial acetic acid was recovered almost quantitatively by diluting the solution with water.

III. Salt Formation

Inasmuch as diphenyl isoxazolone is strongly acidic, there is no difficulty in preparing its salts. Beckmann and Paul[8] analyzed the silver salt and found that its composition corresponds to that of a metallic derivative. Walther and Schickler,[9] unaware of the earlier work, repeated the analysis and reported values corresponding to a salt of the open chained oximido acid. Since then so many salts of other disubstituted isoxazolones have been found to be metallic derivatives that there now can be scarcely any question that the salts of these isoxazolones are formed by replacement of hydrogen by a metal. We analyzed a sample of the silver salt which had been dried at 120° and confirmed the values obtained by Beckmann and Paul, but we also found that the salt tenaciously retains considerable amounts of water. Thus a salt which had been dried to constant weight in a vacuum desiccator gave low values for silver and lost water when heated to 120°. The loss, however, was less than half of that required for a salt of the open chained acid.

In addition to the silver and sodium salts we found the copper acetate and magnesium bromide salts useful, the former as a means of detection and identification and the latter for operations in ethereal solution. For our purpose the sodium salt was made by dissolving 5 g. of the isoxazolone

[8] Ref. 1, p. 20.

[9] Ref. 2, p. 316.

in 50 cc. of saturated sodium carbonate diluted with an equal volume of water. This solution when chilled deposited a hydrated form that melted at 50° and resolidified at 120°. The thoroughly dried salt is very hygroscopic.

The Copper Salt, $C_{15}H_{10}ONOCuOCOCH_3$.—The mixed copper salt was made by shaking an ethereal solution of the isoxazolone with aqueous copper acetate and also by adding the acetate to an aqueous solution of the sodium salt The products are identical. The salt separates as a deep blue or purple crystalline precipitate, As it is insoluble alike in water and in organic solvents it serves well as a means of detecting small quantities of the isoxazolone. For the purpose of analysis it was washed with water and acetone and dried to constant weight.

Anal. Calcd. for $C_{17}H_{13}O_4NCu$: Cu, 17.75. Found: 17.47.

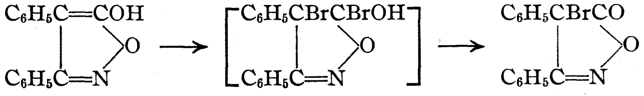
The analysis indicates a mixed salt and the presence of the acetic acid residue was confirmed by warming the salt with alcohol and concentrated sulfuric acid.

The Magnesium Bromide Salt.—An ethereal solution of this mixed salt was made by adding the isoxazolone to an excess of ethyl magnesium bromide and warming the mixture until the evolution of gas ceased. Owing to the insolubility of the isoxazolone in ether the reaction is slow but a quantitative experiment with methyl magnesium iodide in *iso*-amyl ether showed that even after prolonged heating only one molecule of reagent had been consumed and that one molecule of methane was liberated. The ethereal solutions are generally yellow and sometimes they develop a brown color but direct experiment showed that the isoxazolone is recovered quantitatively when the solutions are acidified. The color is doubtless due to a small quantity of iron compounds in the reagent; it disappears on addition of water. No attempt was made to isolate the mixed salt; it was used only in ethereal solution immediately after it had been prepared.

IV. Halogenation and Oxidation

Halogenation and oxidation are grouped together here because diphenyl isoxazolone is so easily oxidized that, unless special precautions are taken, operations intended to give halogen compounds give, instead, large quantities of the oxidation product. For this reason it is best to prepare the chlorine compound by the action of phosphorus pentachloride. The bromine compound can be made by adding bromine to solutions of the ketone but both the bromine and the solvent must be thoroughly dry.

Since the halogen compounds behave neither like hypo halides nor like imine halides they must be derived from the carbonyl form of the isoxazolone. Brominations which are carried out in solutions in which the substance is largely enolic doubtless start with the usual addition reaction



V VIII

4-Bromo-3,4-diphenyl Isoxazolone (VIII).—The finely powdered solid isoxazolone was suspended in dry carbon tetrachloride and treated with a slight excess of bromine which had been distilled from phosphorus pentoxide. The solid dissolved with evolution of hydrogen bromide. The solution, on evaporation under diminished pressure, left an oil that solidified when rubbed with methyl alcohol. After recrystallization from methyl alcohol the solid melted at 72°; yield, 90%. The same bromine compound was formed when dry bromine was added to a chilled ethereal solution of the magnesium derivative. It is not attacked by ozone and it is insoluble in alkalies, but prolonged heating with methyl alcoholic potassium hydroxide destroys it.

Anal. Calcd. for $C_{15}H_{10}O_2NBr$: C, 56.96; H, 3.2. Found: C, 56.66; H, 3.25.

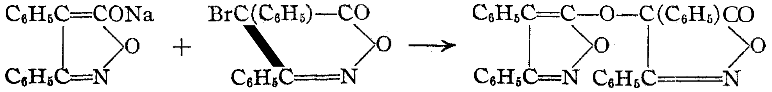
4-Chloro-3,4-diphenyl Isoxazolone.—Three g. of phosphorus pentachloride was added to 3 g. of the isoxazolone suspended in 40 cc. of chloroform. After the vigorous initial reaction had subsided, the mixture was boiled for forty-five minutes, then filtered and evaporated under diminished pressure. It left an oil which was dissolved in ether. The ethereal solution deposited the solid which after purification melted at 77–78°; yield, 50%.

Anal. Calcd. for $C_{15}H_{10}O_2NCl$: C, 66.3; H, 3.7. Found: C, 65.9; H, 3.85.

One of the conspicuous properties of diphenyl isoxazolone is the ease with which it is oxidized. The solid form is stable in the air but its solutions develop color and gradually deposit a sparingly soluble, colorless oxidation product. This is formed rapidly when solutions in suitable solvents are treated with ferric chloride, bromine that has not been carefully dried, nitrous and nitric acids. It is formed also from the sodium salt by such oxidizing agents as bromine, potassium permanganate and potassium ferricyanide. Its composition and molecular weight indicate that its formation involves the removal of two atoms of hydrogen from two molecules of the isoxazolone. In agreement with this it was found that in the oxidation with permanganate only one atom of oxygen is required to oxidize two molecules of the salt and that the product is insoluble in alkalies.

A similar dimolecular oxidation product was obtained by Volhard[10] from 3-benzyl-4-phenyl isoxazolone. From the composition of this substance and its insolubility in alkalies, Volhard concluded that it is formed from two molecules of the "ketonic modification"[1] by removing two atoms of hydrogen and adding one atom of oxygen. The resulting formula seemed to us a *priori* rather improbable. Carbon and hydrogen determinations do not with certainty establish the presence or absence of an additional oxygen atom, but the quantity of permanganate required to form the substance from the sodium salt shows conclusively that the oxygen consumption corresponds to one atom for two molecules of isoxazolone.

Since an ether formed by removing one atom of hydrogen from the carbonyl, the other from the enolic modification would likewise be insoluble in alkalies, we undertook the synthesis of such a compound. We found that the oxidation product can be obtained by the interaction of the bromo compound and the dry sodium salt in absolute ether



IX

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[10] Volhard, *Ann.*, 296, 9 *(1897)*.

While we do not regard this evidence as conclusive, we deem it likely that the oxidation products which are so readily formed from the disubstituted isoxazolones are ethers of the type represented by IX. The process of oxidation thus appears to be quite similar to that of phenols; in alkaline solutions these likewise are readily oxidized to dimolecular products in which one half of the molecule is aromatic, the other half alicyclic.[11]

Preparation.—From the isoxazolone the oxidation product is very easily obtained with nitrous acid. Thus 15 g. of sodium nitrite was added little by little to a solution of 5 g. of the isoxazolone in acetic acid. After the addition the solution was left to itself for forty-five minutes, then made alkaline with sodium carbonate and extracted with ether. The ethereal solution gave 3.6 g. of crude product melting at 148°—a yield of 70%. By the same procedure, nitric acid which had been freed from nitrous acid gave a yield of 60%; as there were no nitro compounds the substance is evidently more easily oxidized than nitrated.

The best method of preparation is by oxidation of the sodium salt. A solution of the isoxazolone in the minimum quantity of half saturated sodium carbonate is treated with finely powdered permanganate until the color persists. The excess of permanganate and the oxides of manganese are removed with bisulfite and acid, leaving the product as a finely divided solid which is easily purified by recrystallization from a mixture of acetone and methyl alcohol; yield, 90%.

The only method of preparation that gave any clue as to the structure of the oxidation product was carried out as follows. Equivalent quantities of the thoroughly dried sodium salt and the bromine substitution product were suspended in dry ether. Reaction is slow and incomplete. The mixture was boiled for ten hours, then filtered. The solid was washed with methyl alcohol to remove unchanged bromo compound and with water to free it from bromide. The crude product melted with decomposition at 152–155° and a mixture of this and the pure substance at 154–156°.

Anal. Calcd. for $C_{30}H_{20}O_4N_2$: C, 76.2; H, 4.3. Found: C, 76.3; H, 4.4.

In boiling acetone the molecular weights found were 467 and 473 instead of 473 calculated for the dimolecular compound.

The oxidation product is sparingly soluble in ether and in methyl alcohol, readily soluble in acetone. It is insoluble in alkalies. On prolonged boiling with methyl alcoholic potassium hydroxide it is altered but does not yield isoxazolone. Towards constant boiling hydriodic acid it shows the normal behavior of an oxygen ether. Thus when 1.18 g. was boiled for two hours with the calculated quantity of acid, it gave 0.4 g. of isoxazolone and an oil that was insoluble in alkalies but readily soluble in organic solvents.

V. Titration with Bromine

The first titrations were made by the procedure which is commonly used for determining by the Kurt Meyer method the quantity of enolic modification in a keto-enol mixture. The isoxazolone was dissolved in about 50 cc. of absolute alcohol, bromine in excess was added to the solution, then β-naphthol and finally potassium iodide. After two to three minutes the liberated iodine was titrated with standard thiosulfate, using the disappearance of the iodine color as end-point, The values are shown in the following table.

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[11] Pummerer, Putffarcken and Schopflocher, *Ber.*, 58, 1808 (1925).

TABLE I

TITRATION VALUES WITH BROMINE

	Substance, g.	Thiosulfate, (0.1026 *N*) cc.	Iodine, g. per mole	Enol, %
1	0.2303	17.20	230.5	90.8
2	.2810	20.50	225.3	88.7
3	.1634	11.82	223.3	87.9
4	.1634	12.30	232.3	91.5
5	.1634	11.80	223.3	87.8

The first two values were obtained in determinations which were parallel except that the first was made at 24°, the second with chilled reagents at −5°. The remaining three values were obtained with an alcoholic solution which had been kept in the dark for fifteen days. Of these three values the last two represent parallel determinations made after adding a drop of dilute hydrobromic acid and allowing the solutions to stand for several minutes. These values indicate that solutions of diphenyl isoxazolone contain about 90% of "enolic" modification and that they reach equilibrium with great rapidity, but before this interpretation could be accepted it was necessary to establish that the missing material could not be accounted for by oxidation or the formation of a bromine compound that is not readily reduced by hydrogen iodide.

For the purpose of determining whether an appreciable amount of oxidation occurs during the titrations we repeated the operation with a larger quantity of material and in the absence of β-naphthol which interferes with the detection of the oxidation product. To a solution of 1.084 g. of the isoxazolone was added first a slight excess of bromine, then potassium iodide in excess. After three minutes the liberated iodine was removed with the dilute thiosulfate, the solution diluted and extracted with ether. The ethereal solution was washed in succession with calcium chloride, half saturated sodium carbonate and water, and then evaporated. It left a small wet residue which was dissolved in 2–3 cc. of methyl alcohol. This solution was inoculated with oxidation product, but beyond a slight cloudiness no solid appeared. Since this procedure should detect at least 0.04 g. of the oxidation product, the titration values are not vitiated by oxidation.

In order to test the rapidity and completeness with which the bromo isoxazolone is reduced by potassium iodide in acid solution, a drop of dilute hydrobromic acid was added to a solution of 0.4471 g. of the bromo isoxazolone. Potassium iodide was then added in excess and after two minutes the liberated iodine was titrated. It required 27.10 cc. of the standard thiosulfate solution, equivalent to 98.25% of the bromo compound.

In view of the rapidity with which the equilibrium is established it seemed improbable that the nature of the solid substance could be established by the Kurt Meyer method but, since no other could be used with a substance having so high a melting point, it was tried. To this end the titrations were repeated with materials purified with great care in apparatus that had been thoroughly steamed immediately before use. The values now were:

TABLE II

Substance, g.	Thiosulfate, (0.1021 N) cc.	Iodine, g. per g. m.	Enol, %
0.1109	6.70	185.6	73.1
.1402	5.49	120.2	47.3
.1903	10.50	185.6	66.7

The variations in the values obtained in such shifting systems are, inevitably, large but the consistently low results show that the solid cannot be the enolic modification.

VI. Alkylation and Acylation

The most interesting reactions of diphenyl isoxazolone are alkylation and acylation. For the study of the former we selected methylation and benzylation. Methylation can be accomplished in a great variety of ways, all of which lead to the same methyl derivative. This was formed when methyl iodide was added to a solution of the isoxazolone in methyl alcoholic sodium methylate, when methyl iodide was allowed to react with the dry sodium salt suspended in benzene or the dry silver salt suspended in ether, by the action of dimethyl sulfate on the sodium salt in water or on the magnesium bromide salt in ether, and by boiling a pyridine solution of the isoxazolone with methyl iodide.

Little is known about the course of alkylation of isoxazolones. Uhlenhuth[12] made the methyl and ethyl derivatives of phenyl isoxazolone from the silver salt. By boiling the methyl compound with alcoholic potash he obtained a small quantity of a volatile base which he caught in hydrochloric acid and turned into a chloroplatinate. The analysis of the chloroplatinate gave a value for platinum from which he concluded that the base was methyl amine and, therefore, that the methylation product was an N-methyl derivative. The evidence seems inconclusive because the value for platinum lies almost exactly midway between that of an ammonium and a methyl ammonium chloroplatinate.

We degraded our methyl derivative in accordance with Uhlenhuth's procedure but obtained only traces of a volatile base—far too little for identification. The principal degradation product was desoxybenzoin but we also obtained a small quantity of benzoic acid. These substances could not arise from a C-methyl but they might be formed equally well from an O-methyl or an N-methyl derivative. A Zeisel methoxyl determination which gave a negative result eliminated the oxygen ether and ozonization finally supplied positive evidence that the substance is an N-methyl ester. The degradation with bases doubtless is represented by the

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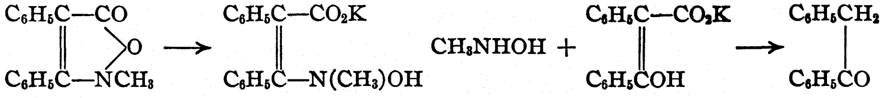
[12] **Uhlenhuth, ref. 4, p. 46.**

following scheme which shows that methyl amine, if formed at all, would be a secondary product.



X

N-Methyl-3,4-diphenyl Isoxazolone (X).—For preparing the ether in quantity we prefer the following method. The isoxazolone (47.4 g.) was dissolved in 120 cc. of methyl alcoholic sodium methylate containing 7 g. of sodium. To this solution was added 56.8 g. of methyl iodide. The mixture was boiled until neutral, then made strongly alkaline with sodium methylate and while still hot diluted with much water. On cooling it deposited 27 g. of the methyl derivative, and ether extracted 4 g. more. The alkaline solution contained 16 g. of unchanged isoxazolone which was recovered by acidification; yield, 91%. The ether was purified by recrystallization from ether and petroleum ether, or methyl alcohol and water. It crystallizes in needles and melts at 92°.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.5; H. 5.2. Found: C, 76.4; H, 6.3.

The methyl ether was not affected by heating for twelve hours at 110–115° with concentrated hydrochloric acid, and heating with hydriodic acid in the Zeisel apparatus gave no methyl iodide. It was insoluble in aqueous alkali but when boiled with strong methyl alcoholic potassium hydroxide for two hours, 1.8 g. left an oil from which 0.5 g. of pure recrystallized desoxybenzoin and 0.1 g. of benzoic acid were extracted.

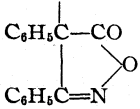
Ozonization.—Ozonized oxygen containing about 6% of ozone was passed for 3 hours through a solution of 2.6 g. of the methyl ether in 35 cc. of carbon tetrachloride. The solvent was removed under diminished pressure and the ozonide first treated with water, then warmed with dilute sodium hydroxide and finally distilled with steam in order to remove nitrogenous products. From the residue ether extracted a small quantity of unchanged substance. The alkaline layer was acidified and treated with phenyl hydrazine. It deposited the phenyl hydrazone of benwyl formic acid, which was identified by comparison with a sample on hand.

The N-benzyl Ether.—The benzyl derivative was made in the hope that it might be more suitable for studying the action of bases on the N-alkyl derivatives. This proved not to be the case. It melts at 123' and its behavior towards alkalies and ozone is exactly like that of the methyl derivative.

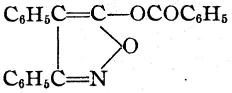
Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.7; H, 5.2. Found: C, 80.4; H, 5.3.

Acylation was first studied with benzoyl chloride and then, since ozonization of the benzoate did not clearly exclude the possibility that the acyl group might go to carbon atom 4, it was repeated with chloro formic ester, which almost invariably forms O-acyl derivatives. Benzoylation in pyridiie, in water by the Schotten-Baumann reaction, and in ether by the action of benzoyl chloride on the magnesium bromide derivative gave the same benzoate.

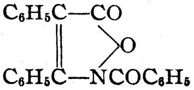
It is difficult to secure absolutely explicit evidence as to the structure of the acyl derivatives. The three possible formulas of the benzoate are



XI



XII



XIII

The third of these formulas is definitely excluded by the results of ozonization. A substance with this structure should, like the ethers, form an ozonide which on decomposition with water would give phenyl glyoxylic acid as one of the products. The benzoate does not form an ozonide. It is slowly attacked by concentrated ozone, but no treatment of the resultant oil yields even a trace of phenyl glyoxylic acid which can be detected with the very delicate color reaction of this substance.

A substance with the structure represented by XII would be expected to behave towards ozone essentially like triphenyl isoxazol which, as has been shown by Meisenheimer,[13] can be oxidized to a derivative of benzilmonoxime. Despite many attempts we were never able to isolate benzil, its monoxime or any other definite oxidation product. The experiments with ozone, therefore, do not serve to distinguish between formulas XI and XII. There remains only the behavior towards hydrolytic agents. Both acids and bases regenerate the isoxazolone much more easily than they would be expected to hydrolyze a substance like that represented by XI. Indeed, one would be inclined to predict that the primary action of strong bases on such a substance would be ring-opening, and that the final product would be triphenyl isoxazol. In the absence of more explicit evidence, however, the detailed structure of the acylation products of isoxazolones must be regarded as unknown.

The Benzoate.—The crude benzoate obtained in pyridine or by the Schotten-Baumann reaction melted at 126–127°, while that from the magnesium bromide derivative melted at 135°. It was at first suspected that the lower-melting preparation might contain isomeric benzoates, but careful fractional crystallization failed to disclose such isomerism. The benzoate crystallizes well both from ether and from alcohol in needles melting at 138–139°.

Anal. Calcd. for $C_{22}H_{15}O_3N$: C, 77.4; H, 4.4. Found: C, 77.5; H, 4.4.

The Ethyl Carbonate.—Twice the calculated quantity of chloro carbonic ester was added to 5 g. of the dry sodium salt suspended in absolute ether. The mixture was boiled for an hour, then poured into water. The ethereal layer, washed with sodium carbonate and water, dried and evaporated, gave 4.3 g. of ester—a yield of 85%.

Anal. Calcd. for $C_{18}H_{15}O_4N$: C, 69.9; H, 4.9. Found: C, 69.8; H, 4.9.

The ester crystallized well but always softened at 103° before it melted at 109–110°. The ester was rapidly hydrolyzed by bases, yielding 90% of isoxazolone after it had been heated for fifteen minutes with methyl alcoholic potassium hydroxide. Its behavior towards ozone was precisely like that of the benzoate.

Summary

The paper contains a method for preparing 3,4-diphenyl isoxazolone in quantity and an account of the experiments made for the purpose of establishing the structure of the solid form, the equilibrium in solution and the structure of the bromination, acylation and alkylation products.

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[13] Meisenheimer, *Ber.*, 54, 3211 (1921).

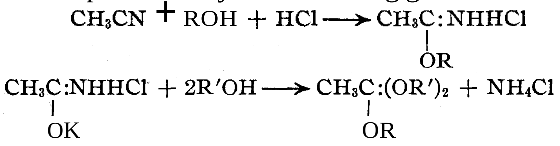
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

ESTERS OF ORTHO-ACETIC ACID[1]

BY PETER P. T. SAH

RECEIVED OCTOBER 15, 1927 PUBLISHED FEBRUARY 4, 1928

Although a number of esters of orthoformic acid, simple and mixed, were prepared by Pinner[2] through the action of alcohols on form-imino-ether hydrochlorides, their corresponding homologs, the various esters of ortho-acetic acid, with the exception of triethyl ortho-acetate, were not described in the literature. This only known ester of ortho-acetic acid was first synthesized by Geuther[3] in 1871 from methyl chloroform and sodium ethoxide. Since methyl chloroform is hard to prepare in available amounts in the laboratory, this method is only of theoretical interest. In 1907, Reitter and Hess[4] allowed ethyl alcohol to react with Pinner's acet-imino-ethyl-ether hydrochloride and isolated triethyl ortho-acetate. The reaction was not further developed and the various esters of ortho-acetic acid remained unknown. It is the purpose of this communication (1) to relate how triethyl ortho-acetate was prepared in large quantities in the laboratory by a simplified and improved procedure of Reitter and Hess and (2) to describe a few simple physical constants of the various new ortho-acetates produced by the following general reaction



$$CH_3CN + ROH + HCl \longrightarrow \underset{OR}{\underset{|}{CH_3C}}{:}NHHCl$$

$$\underset{OK}{\underset{|}{CH_3C}}{:}NHHCl + 2R'OH \longrightarrow \underset{OR}{\underset{|}{CH_3C}}{:}(OR')_2 + NH_4Cl$$

Experimental Part

Acet-imino-ethyl-ether Hydrochloride.[5]—This was prepared according to Pinner's method. Into a cooled mixture of anhydrous acetonitrile (135 g., b. p. 82°), absolute ethyl alcohol (200 cc.) and absolute ether (120 cc.), there was introduced a slight molecular excess of dry hydrogen chloride. This mixture, after standing in the icebox overnight, solidified into a hard cake of white, shining plates. The ether was decanted. The hydrochloride was dried in a vacuum over soda lime for twenty-four hours to remove the excess of hydrogen chloride; yield, 86–95%. By using methyl alcohol in place of ethyl alcohol in the above reaction, acet-imino-

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[1] This paper was constructed from a thesis submitted by Peter P. T. Sah to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 21, 1926. The investigation was carried out under the direction of Professor Richard Fischer.

[2] Pinner, *Ber.*, **16**, 1644 (1883).

[3] Geuther, *Zeitschrift für Chemie*, **1871**, *128*.

[4] Reitter and Hess, *Ber.*, 40, 3020 (1907).

[5] Hill and Rabinowitz, THIS JOURNAL, 48, 732 (1926).

methyl-ether hydrochloride was obtained as white, shining plates; yield, 71.6%.

Triethyl Ortho-Acetate.—Three hundred and fifty g. of acet-imino-ethyl-ether hydrochloride, absolutely dry and free from hydrogen chloride, was treated with 750 cc. of absolute ethyl alcohol. The mixture was allowed to stand in a tightly stoppered bottle in a dry place for two weeks with occasional shaking. The ammonium chloride separating out was filtered. This was preserved, since the reaction of alcohol with imino-ether hydrochloride was very slow and the solid precipitate still contained a large amount of the unreacted hydrochloride. The filtrate was treated with 2 g. of fused potassium carbonate to remove any trace of free hydrogen chloride. The solution was then fractionated under reduced pressure of 40–60 mm. The first fraction boiled over between 25 and 35°, consisted of absolute alcohol with some ortho-acetate and was used again in the further treatment of the precipitate of ammonium chloride as well as the fresh portion of acet-imino-ethyl-ether hydrochloride. The fraction from 55 to 75° at 50 mm. was collected and refractionated at atmospheric pressure. Pure triethyl ortho-acetate boiled very constantly at 144 to 146° at atmospheric pressure without any decomposition. Prom four runs 750 cc. of pure product was obtained.

TABLE I

PREPARATION AND ANALYSIS OF ORTHO-ACETATES

Formula	Synthetic reagents	Analysis			% H		% C	
		Subs., g.	H_2O, g.	CO_2, g.	Calcd.	found	Calcd.	found
$CH_3C(OCH_3)_3$	$CH_3C{:}NHHCl$	0.1009	0.0914	0.1844	10.07	10.14	49.96	49.84
	$\vert$	.1012	.0922	.1862		10.19		50.18
	OCH_3	.1017	.0918	.1857		10.10		49.80
or $C_5H_{12}O_3$	$+2CH_3OH$							
$CH_3C(OCH_3)_2$	$CH_3C{:}NHHCl$	.1014	.0952	.1988	10.52	10.51	53.69	53.47
$\vert$	$\vert$	.1028	.0964	.1990		10.49		52.79
OC_2H_3	OC_2H_5	.1025	.0967	.2002		10.55		53.27
or $C_6H_{14}O_3$	$+2CH_3OH$							
$CH_3C—OCH_3$	$CH_3C{:}NHHCl$	.0946	.0985	.1967	10.89	11.65	56.71	56.71
$\Vert$	$\vert$	.1006	.0976	.2088		10.86		56.61
$(OC_2H_5)_2$	OCH_3	.1013	.0982	.2106		10.84		56.70
or $C_7H_{16}O_3$	$+2C_2H_5OH$							
$CH_3C—OC_2H_5$[6]	$CH_3C{:}NHHCl$	.0950	.1004	.2232	11.66	11.83	63.10	64.08
$\Vert$	$\vert$	.0943	.0999	.2222		11.86		64.26
$(OC_3H_7)_2$	OC_2H_5	.1042	.1098	.2445		11.79		63.99
or $C_{10}H_{22}O_3$	$+2C_3H_7OH$							
$CH_3C—OC_2H_5$[6]	$CH_3C{:}NHHCl$	.1002	.1148	.2457	12.01	12.82	65.99	66.88
$\Vert$	$\vert$	.1496	.1735	.3678		12.98		67.05
$(OC_4H_9)_2$	OC_2H_5	.1150	.1343	.2816		13.07		66.78
or $C_{12}H_{26}O_3$	$+2C_4H_6OH$							

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[6] The slightly high values of molecular refraction and carbon content of these two ortho-esters seemed to indicate that they were contaminated, respectively, by traces of **tri-*n*-propyl** and tri-n-butyl ortho-acetates from which they could not be separated by fractional distillation.

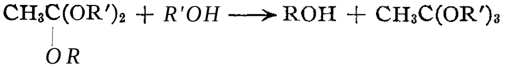
TABLE II

PHYSICAL PROPERTIES OF ORTHO-ACETATES

Ortho-acetates	B. p., °C.	d_4^{25}	n_D^{25}	Mol. ref. (G. and D.) Obs.	Calcd.	Mol. ref. (L. and L.) Obs.	Calcd.
Trimethyl	107–109	0.94375	1.38585	49.10	49.14	29.88	30.166
Dimethylethyl	123–126	.91915	1.38885	56.73	56.79	34.49	34.769
Methyldiethyl	135–136	.90085	1.39185	64.43	64.44	39.14	39.372
Ethyldi-*n*-propyl[6]	190–194	.87129	1.40635	88.70	87.39	53.66	53.181
Ethyldi-*n*-butyl[6]	220–225	.86461	1.41485	104.70	102.69	63.18	62.387

The ester is a colorless liquid with a pleasant odor, similar to that of ethyl acetate but stronger. The following constants were noted: b. p. 144–146°; n_D^{25}, 1.39485; d_4^{25}, 0.8847; molecular refraction (Gladstone and Dale), 72.33 (obs. val.), 72.09 (calcd. val.); molecular refraction (Lorenz and Lorentz), 43.91 (obs. val.), 43.975 (calcd. val.). The liquid is insoluble in cold water, but is miscible with ethyl alcohol, ether, ethyl acetate, chloroform and carbon tetrachloride. It is highly volatile with ethyl alcohol when distilled with the latter at atmospheric pressure.

By allowing various alcohols to react with acet-imino-ether hydrochloride, five new esters of ortho-acetic acid were isolated. Their method of preparation and physical properties are described in the following tables. In the case of a higher alcohol reacting on a lower alcohol derivative of imino-ether hydrochloride, there was always observed, in perfect accord with Pinner's experiments,[2] the formation of a by-product, a simple ortho-ester, in small amounts. The lower alcohol radical had a tendency toward being replaced by the higher alcohol, which was in excess.



$$\underset{\displaystyle |\atop OR}{CH_3C}(OR')_2 + R'OH \longrightarrow ROH + CH_3C(OR')_3$$

Summary

1. A simple procedure for the preparation of triethyl ortho-acetate is described.

2. Five new esters of ortho-acetic acid were prepared through similar reactions and their physical constants studied

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

THE PREPARATION AND PROPERTIES OF *l*-MANNONIC AND *l*-GLUCONIC LACTONES[1,2]

BY FRED W. UPSON, LILA SANDS AND CARRELL H. WHITNAH

RECEIVED OCTOBER 17, 1927 PUBLISHED FEBRUARY 4, 1928

Pischer[3] first prepared crystalline *l*-mannonic lactone from d-arabinose while van Ekenstein and Blanksma[4] isolated it later in the preparation of *l*-mannose.

The *l*-gluconic acid was isolated by Fischer in the form of a sirup. Nef[5] and also Hedenburg[6] prepared two crystalline modifications of d-mannonic lactone and also of d-gluconic lactone. The two modifications of d-mannonic lactone are fully described by Hedenberg.[6] One, which is undoubtedly the γ-lactone, possesses an initial specific rotation of $+51.8°$ in water and melts at 151°. The rotation changes only very slowly. The second lactone possesses an initial rotation of $+111.8°$ which diminishes very rapidly in water solution to a value of $+84.8°$ in less than two hours and to $+29.5°$ at the end of twenty-six hours Hedenburg gave to this lactone provisionally a propylene oxide structure. As shown in another part of this paper this lactone should be formulated in all probability as an amylene oxide or 6-lactone.

The present paper gives an account of the properties of the corresponding lactones of *l*-mannonic and *l*-gluconic acids prepared from *l*-arabinose by the Kiliani reaction. *l*-Gluconic acid lactone has been prepared for the first time in a crystalline state and a tetramethyl mannonic acid lactone prepared and its properties determined.

Experimental Part

Addition of Hydrogen Cyanide to *l*-Arabinose.—*l*-Arabinose was treated with hydrogen cyanide according to the directions of Fischer.[3] The resulting nitriles were converted to the mixed acids by the usual process through hydrolysis with barium hydroxide. The sirup obtained after precipitation of the barium as sulfate yielded two fractions (A) of nearly pure crystalline *l*-mannonic lactone. The residual sirups were thoroughly extracted with absolute alcohol, leaving behind a thick, colloidal residue. The alcoholic extracts yielded two more fractions (B) of crystalline products which were mixtures of *l*-mannonic and *l*-gluconic lactones. The filtrates (C) resulting here were converted to the brucine salts and yielded crude brucine *l*-gluconate, from

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[1] Presented before the Organic Division of the American Chemical Society at the Washington Meeting, April, 1924; abstract in *Science*, 60, 49 (1924).

[2] Constructed from theses presented by Lila Sands and Carrell H. Whitnah in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Nebraska in 1924 and 1925, respectively.

[3] Fischer, *Ber.*, 23, 273 (1890).

[4] Van Ekenstein and Blanksma, *Chem. Weekblad.*, 11, 902 (1914).

[5] Nef, *Ann.*, 403, 309 (1914).

[6] Hedenburg, THIS JOURNAL, 37, 345 (1915).

which crystalline *l*-**gluconic lactone** was first obtained. The various fractions of brucine salt were subjected to fractional crystallization either from water or alcohol. There were obtained from **100** g. of I-arabinose **58.8** g. of pure I-mannonic **lactone** and **8.8** g. of crystalline *l*-**gluconic lactone.** Fischer obtained a yield of 40 g. of *l*-**mannonic lactone,** but *l*-**gluconic lactone** was isolated only in sirupy form.

l-Mannonic Lactones

***l*-Mannonic-γ-lactone.**—The crystalline fractions **(A)** described in the first part of this paper, which consisted of almost pure 1-mannonic **lactone,** were purified by recrystallization from absolute alcohol and then glacial acetic acid and converted to the γ-**lactone** according to the procedure of **Nef.**[5] **A** pure white crystalline **lactone** melting sharply at 150.5–151° and possessing a specific rotation of **—51.8'** was obtained. No significant change in rotation occurred during a period of two days.

Titration.—The **lactone** reacted very slowly with alkali at room temperature and required a temperature of approximately 100° to complete the titration.

Anal. **0.2064** g. required **11.85** cc. of **0.0972** *N* NaOH; calcd. for $C_6H_{10}O_6$: **11.93** cc. Calcd. for $C_6H_{10}O_6$: H, **5.61; C, 40.45.** Found: H, **5.57;** C, **40.69.**

The properties of this **lactone** show it to be the enantiomorph of the d-mannonic γ-**lactone** obtained by Nef and by Hedenburg. The fact that neutralization proceeds very slowly at room temperature and also the slow change in rotation prove that these lactones, the one a d- and the other an *l*-**mannonic lactone,** possess in all probability the stable or butylene oxide structure.7

Tetramethyl-*l*-mannonic γ-Lactone.—The *l*-mannonic 7-lactone obtained as described above was methylated by means of methyl iodide and silver oxide according to the method of Purdie and **Irvine.**[8] The process required two treatments with methyl iodide and silver oxide using methyl alcohol as a solvent and a further treatment with methyl iodide as the solvent. This process gave a tetramethyl *l*-**mannonic** methyl ester. The ester group was hydrolyzed by boiling for half an hour with a slight excess of **0.5** N sodium hydroxide. Hydrochloric acid exactly equivalent to alkali was added and the whole distilled under **reduced** pressure to complete dryness at 100°. The methylated **lactone** was extracted from the sodium chloride with ether and the ether solution dried. Upon evaporation this solution deposited the methylated **lactone** in a crystalline condition. This compound was shown by analysis to be a tetramethylated **lactone.**

Titration.—The compound **titrated** like a **lactone,** that is, only a very small amount of alkali was taken up at room temperature and complete neutralization could be accomplished only on heating to 100°.

Anal. **0.1820** g. required **7.43** cc. of **0.103** N NaOH. Calcd. for $C_{10}H_{18}O_6$: **7.54** cc. Calcd. for $C_{10}H_{18}O_6$: H, **7.71;** C, **51.28.** Found: H, **7.8;** C, **50.88.**

Methoxyl determination: Calcd. for $C_{10}H_{18}O_6$: methoxyl, **52.99.** Found: **53 7.**

This tetramethyl *l*-**mannonic lactone** crystallizes in long, narrow, colorless plates which melt at 109°. It is readily soluble in ether and alcohol, less soluble in water.

The specific rotation in water solution six minutes after solution was **—65.51';** after thirty-four hours −64.11°; while at the end of five days the rotation had changed to −60.6°, becoming constant after eighteen days with $[\alpha]^{20}_{D} = -47.4'$. This slow change in specific rotation, together with the fact that the titration could not be com-

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[7] Pryde, **J** *Chem. Soc.*, *123,* **1811 (1923).**

[8] Purdie and Irvine, **J.** ***Chem. Soc.*, *83,* 1026 (1903).**

pleted at 25°, is evidence that the compound possesses the butylene oxide or γ-lactone structure.

Tetramethyl *d*-Mannonic γ-Lactone.—For purposes of comparison this compound was prepared by direct methylation of d-mannonic y-lactone, m. p. 151'. The methylation was carried out using methyl iodide and silver oxide as already described for the *l*-mannonic lactone. The compound was obtained in the form of colorless plates; m. p. 107°.

Anal. Methoxyl determination, calcd. for $C_{10}H_{18}O_6$: methoxyl, 52.99. Found: 52.34.

Titration.-4.2120 g. required 9.1 cc. of 0.1 *N* NaOH. Calcd. 9.05 cc. The specific rotation of this compound in water solution was found to be +66.6° immediately after solution. After six hours the value was +64° and after twenty-four hours +63°. A graph in Fig. 1 shows the change of rotation with time.

The High Rotating Mannonic Lactones.—Hedenburg,[6] by the action of oxalic acid on calcium d-mannonate, prepared a second lactone of d-mannonic acid, characterized by a high initial specific rotation of +111.8° which diminished in the course of twenty-six hours to the value of +29.3°. This lactone also was neutralized much more readily with alkali. These facts indicate an unstable lactone and led Hedenberg to formulate it as a propylene oxide or β-lactone. The evidence obtained in this investigation leads to the conclusion that this lactone is in all probability an amylene oxide or δ-lactone.

The Active *l*-Mannonic Lactone.—This lactone was prepared according to Hedenburg's method and found to consist of microscopic, colorless plates which melt at 160–162°.

And. Calcd. for $C_6H_{10}O_6$: H, 5.62; C, 40.45. Found: H, 5.71; C, 40.68. The substance titrated more readily than did the y-lactone; 0.1020 g. required 5.5 cc. of 0.103 *N* NaOH. Calcd. for $C_6H_{10}O_6$: 5.6 cc.

The lactone in aqueous solution has a high initial specific rotation, −113.6°, this diminishing to the value −102.5 after an hour and twenty minutes. At the end of three and one-half hours the value had become −78.5°. At the end of thirty-two and one-half hours the minimum value of −30.9' was reached, after which it slowly increased to the value −40.9 after twenty-eight days. The change in rotation of this I-mannonic lactone is thus shown to parallel the change of rotation of the active d-lactone as observed by Hedenberg. A curve in Fig. 1 shows more concretely the nature of the change.

Active Tetramethyl *d*-Mannonic Lactone.—Tetramethyl *d*-mannose was prepared according to the method of Haworth[9] by means of methyl sulfate and sodium hydroxide. This compound was oxidized by means of bromine as described by Pryde.[10] After removal of hydrobromic acid by means of lead carbonate and silver oxide in the usual way, the methylated oxidation product was extracted with ether and the ethereal solution subjected to fractionation finally at a pressure of 1–2 mm. The tetramethyl d-mannonic lactone was obtained as a colorless oil which showed no tendency to crystallize.

Anal. Calcd. for $C_{10}H_{18}O_6$: H, 7.77; C, 51.28; methoxyl, 52.99. Found: H, 7.76; C, 50.62; methoxyl, 52.83.

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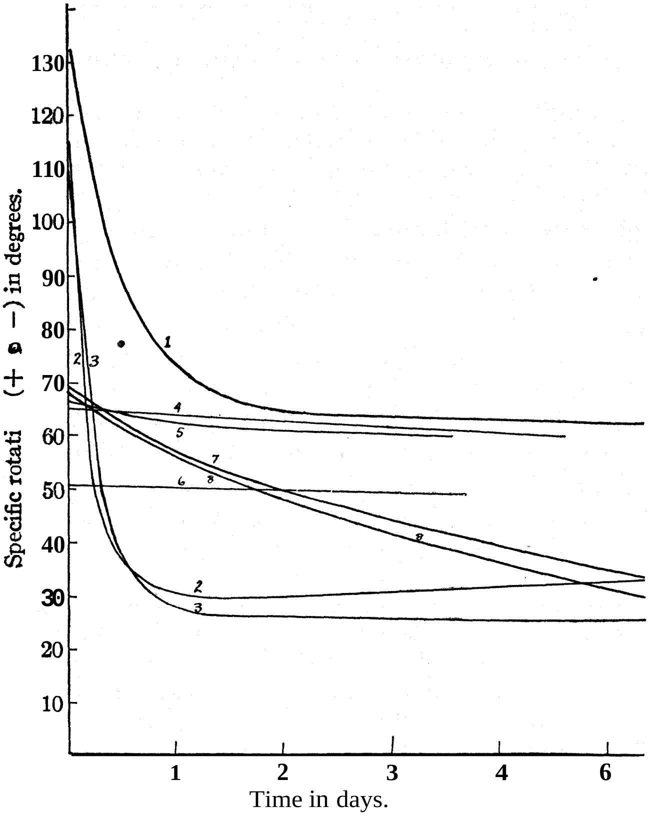
[9] Haworth, J. Chem. *Soc.*, 107, 8 (1915).

[10] Ref. 7, p. 1808.

The titration proceeded rapidly in the cold until about three-fourths complete; 0.2282 **g.** required **9.75** cc. of **0.0972** *N* **NaOH;** calcd. for $C_{10}H_{18}O_6$, **9.9 cc.**

The **initial** specific rotation five minutes after solution was +132.3°. The specific rotation diminished rapidly, changing to the value **+113.6°** after four and one-half hours and to **−76.3'** after twenty-two hours. It reached a minimum value of +59.5°



1. Tetramethyl d-mannonic 8-lactone; **2.** d-mannonic δ-lactone; 3. I-mannonic δ-lactone; **4.** tetramethyl d-mannonic y-lactone; **5.** tetramethyl Lmannonic γ-lactone; **6.** *d*-mannonic and *l*-mannonic γ-lactones; 7. I-gluconic y-lactone; 8. d-gluconic y-lactone.

Fig. 1.--Curves showing change of rotation of various lactones with time.

after about six days and at the end of nine days the value had become +63.6°. A curve in Fig. **1** shows more concretely the change of rotation with time. An inspection of the graph brings out the fact that the curves belong to two distinct types. Those belonging to the normal lactones of d- and *l*-mannonic acids, as well as the methylated derivatives, are almost horizontal and show little falling off. The rotations of the two abnormal lactones and of the methoxyl derivative of the *d*- variety have a much higher initial value and the slope of the curves is very steep at first, becoming more nearly horizontal after twenty hours.

Structure of the Active Mannonic Lactones.—The common lactones of the sugar acids are formulated as butylene oxides of γ-lactones because of their comparative stability towards alkalies and because of the slow change in rotation which they undergo in water solution. Evidence of this view is presented by Hedenberg[6] and by Pryde,[7] and the theory is further supported by Hudson's rule.[11]

According to the rule of Hudson the position of the lactone bridge in the sugar acid lactones determines the sign of rotation. Pryde has shown in the case of galactonic lactone that the two tetramethyl derivatives, the one obtained by the oxidation of methylated galactose and the other by direct methylation of the lactone, differ in sign of rotation. According to Hudson's rule the 1-5 lactone should rotate to the right and the 1-4 to the left. In the case of the lactones of mannonic acid both the 1-4 and the 1-5 should be dextro-rotatory. It seems certain, therefore, that the active d-mannonic lactone of Nef and Hedenburg as well as the active *l*-mannonic lactone here reported together with the tetramethyl lactone obtained by oxidation of tetramethyl mannose, all possess the amylene oxide or 1-5 lactone structure. This leads logically to the conclusion that crystalline mannose possesses the amylene oxide or 1-5 lactone structure. Levene and Meyer[12] have reached the same conclusion based on a study of these same methylated lactones. The constants of their tetramethyl 1,4-lactone agree closely with those determined by us. The second compound of Levene and Meyer, obtained on oxidation of tetramethyl mannose, shows a lower specific rotation, +105°, than the value found in this Laboratory, +132°. It is possible that their product contained some free acid, which accounts for the lower rotation. They give no data showing the change of rotation with time.

Lewis and Greene[13] have recently prepared tetramethyl mannose in a crystalline form. From this they have obtained by oxidation with bromine a tetramethyl lactone in the form of a sirup which shows an initial specific rotation of +136.4° and a final value of +62.4°. These results correspond closely with those found in this Laboratory and their lactone is undoubtedly identical with the one reported above.

It should be noted that Nef[14] in 1914 first suggested that other lactone bridges than those of the γ or butylene oxide type are possible among the members of the sugar group and that Nef and also Hedenburg[6] were the first to obtain representatives of these abnormal lactone types in their studies of mannonic and gluconic lactones. The methylation studies on the mannonic lactones both in this Laboratory and elsewhere connect

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[11] Hudson, THIS JOURNAL, **32, 338** (1910).

[12] Levene and **Meyer,** *J. Biol. Chem., 60,* 167 (1924).

[13] **Lewis** and **Greene,** *Science,* **64,** 206 (1926).

[14] **Ref.** 5, **p. 317.**

definitely the one lactone type of the acid with that of its parent sugar. As pointed out by Charlton, Haworth and Peat,[15] the normal lactone type of the sugar apparently belongs to the γ or amylene oxide form, while the stable normal lactones of the monobasic sugar acids belong to the γ or butylene oxide type. In only one other case, that of glucose, has the unmethylated acid lactone been obtained which corresponds to the normal lactone type of the sugar.[16]

l-Gluconic Lactone

l-Gluconic lactone, as already indicated in the first part of this paper, has been isolated for the first time in a crystalline condition. The mother liquors (C) obtained as already described, from which no more crystalline mannonic lactone could be obtained were converted to brucine salt in the usual way. On crystallization of the brucine salts from absolute alcohol, several fractions melting at temperatures ranging from 150–180° were obtained. As the larger portion of the mannonic lactone had already been removed by crystallization, the crystalline brucine salts obtained here contained very little brucine *l*-mannonate. The whole of the crystalline brucine salt was converted to the free lactone in the usual way through treatment with barium hydroxide and subsequent removal of the barium through precipitation as sulfate. The gluconic lactone was obtained first as a thick gum which showed evidence of crystallization after standing for some days under absolute alcohol. On long standing there was obtained a considerable quantity of crystalline lactone, which could be removed by filtration with vacuum. After the lactone was once obtained it was readily recrystallized from absolute alcohol or glacial acetic acid. The latter solvent was found to give a pure product. The lactone was obtained in the form of colorless plates melting at 134–135°. The initial specific rotation in 3.79% solution was −68.7°. The rotation diminished to the value of −62.5° after twenty-four hours, to the value −58.2° after two days and continued to diminish for some days. The minimum value −13.7' was reached after a period of fifteen days, after which there was a slow increase in the value. This change in rotation closely paralleled that for the d-gluconic lactone as recorded by Hedenburg,[6] who found an initial value of −67.2'.

Titration.-4.2017 g. of lactone required 11.24 cc. of 0.0972 N NaOH; calcd., 11.48 cc.

A number of derivatives of *l*-gluconic lactone were prepared. Two g. of lactone was converted to the brucine salt. After recrystallization from 90% alcohol and drying in *vacuo* the salt melted sharply at 181–182°; $[\alpha]^{20}_{\mathrm{D}} = -25.43$ in 4.01% solution.

The brucine salt of Lmannonic acid was also prepared for purposes of comparison. Its melting point was found to be 161–162° and $[\alpha]^{20}_{\mathrm{D}} = -15.78$" in 3.98% solution.

The phenylhydrazide of *l*-gluconic acid was prepared in the usual way. On recrystallization from water it melted sharply at 200" and $[\alpha]^{20}_{\mathrm{D}} = -11.7$' in water solution of 2.97%. The melting point of the hydrazide of d-gluconic acid is 200° and the specific rotation is +12". The results recorded above indicate very definitely that the compound is the phenylhydrazide of I-gluconic acid. The properties of the lactone, together with those of its brucine salt and phenylhydrazide, indicate clearly that the above-described compound is the crystalline lactone of *l*-gluconic acid.

Summary

1. The lactones of I-mannonic and I-gluconic acids were prepared from I-arabinose in a somewhat better yield than had been obtained previously.

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[15] Charlton, Haworth and Peat, *J. Chem. Soc.*, **129**, 97 (1926).

[16] Ref. 5, p. 323.

2. Two lactones of l-mannonic acid were prepared: the common lactone having a butylene oxide ring and the less stable lactone having an amylene oxide ring.

3. Evidence for the structure of the two lactones was substantiated by the preparation of two distinct tetramethyl mannonic lactones.

4. *l*-Gluconic lactone was prepared for the first time in crystalline form and its constants were determined.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHTS OF PHYCOERYTHRIN AND OF PHYCOCYAN

BY THE SVEDBERG AND N. B. LEWIS[1]

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Phycoerythrin and phycocyan are closely related proteins of the globulin type which occur together in certain algae. They are both fluorescent and have characteristic colors; the color and fluorescence are quite strong even in 0.01% solution. On account of this strong light absorption both in the visible and the ultraviolet and of the relative ease of preparing them in a pure crystalline state they appeared to be particularly suitable for molecular weight determinations by means of the ultracentrifuge.

There is a series of references in the literature to these substances dating back to that of Kützing;[2] but they appear to have first been prepared in a pure state by Kylin.[3] In this paper he gives an account of their preparation from *Ceramium rubrum*, of their chemical properties, absorption spectra and a quantitative analysis of phycoerythrin. It also includes a complete list of the earlier references.

Kitasato[4] used another alga, *Porphyra tenera* (the sun-dried material being an article of commerce in Japan) as raw material, and the substances were prepared by a method analogous to that of Kylin. His observations in general, and his analysis of phycoerythrin, agree with those of Kylin. Further, he was able to make an analysis of phycocyan, which occurs in much smaller quantities (Ceramium *rubrum*, according to Kylin, about $^1/_{10}$ of that of phycoerythrin); his figures for this are very close to those for phycoerythrin.

Experimental

Preparation of Material.—*Ceramium rubrum* was extracted with water as described by Kylin. The extract, consisting of a solution of the mixed substances as well as

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[1] Fellow of the International Education Board.

[2] Kützing, *Phycologia Generalis*, Leipzig, 1843.

[3] Kylin, *Z. physiol. Chem.*, 69, 169 (1910).

[4] Kitasato, *Acta Phytochimica*, 2, 75 (1925).

numerous impurities (slimy carbohydrates, etc.), was treated with about 20% of its weight of ammonium sulfate. The proteins thus precipitated were brought into solution by washing with distilled water. This solution was then treated with increasing amounts of ammonium sulfate up to 20% of its weight. After each addition it was allowed to stand for a day, filtered and the precipitate redissolved. In this way were formed four fractions with differing relative amounts of the two substances. The first fraction (the largest), consisting mainly of phycoerythrin, was recrystallized until the resulting crystals, as seen under the microscope, were seen to be entirely free from phycocyan; and the third and fourth, consisting almost entirely of phycocyan, recrystallized until they were free from phycoerythrin. The precipitate from Fraction 2, consisting of a mixture in which phycoerythrin predominated, was shaken with a little water and centrifuged. The deposit was found to be free from phycoerythrin crystals, which evidently dissolve more rapidly. The various mother liquors obtained, if dilute were discarded, if not, were separated into fractions in a similar manner. As these substances are decomposed on exposure to daylight, the liquids in all cases were kept in the dark, with toluene added as a preservative.

The pure crystalline substances were dissolved in as small a quantity of water as possible and dialyzed in collodium bags against water at 0° for periods of not less than a week, at the end of which time the specific conductivity at 20° had fallen to less than 10^{-4} ohm^{-1}, and the substances had commenced to precipitate in an amorphous form. The phycocyan was dissolved in a dilute sodium phosphate-potassium phosphate buffer solution (PH = 7.0). The phycoerythrin dissolved again when the liquid was poured into a glass vessel (due probably to traces of alkali from the glass). This solution was filtered and part kept without buffer; the remainder in phosphate buffer (PH = 6.8).

Specific Volume.—The partial specific volume at 19.4° of phycoerythrin was determined pycnometrically. The concentration of the sample was determined by drying to constant weight at 105°. The value for a dilute (0.84%) solution was found to be 0.746 which is very close to

TABLE I

EXTINCTION COEFFICIENTS ($\epsilon = 1/d \log I_0/I$) for PHYCOERYTHRIN (0.0097% SOLUTION)

Wave length, μμ	e	Wave length, μμ	ε	Wave length, μμ	ε
635	0.0062	547	0.6565	496	0.6391
605	.0097	541	.6893	492	.5322
579	.2250	538	.6834	479	.3093
574	.5292	533	.6676	468	.1950
569	.7226	521	.5184	457	.1152
565	.7426	514	.4499	438	.0437
561	.6717	506	.5101	422	.0433
557	.6267	499	.6388	404	.0622

TABLE II

EXTINCTION COEFFICIENTS FOR PHYCOCYAN (0.0293% SOLUTION)

λ	a	λ	e	λ	●
691	0.084	605	1.113	530	0.540
671	.125	593	0.856	521	.430
635	.758	579	.757	506	.312
632	.980	567	.787	485	,227
627	1.172	557	.894	457	.146
619	1.271	549	.895	415	.083
611	1.270	538	.792		

that for egg albumin and hemoglobin. For phycocyan, concentration was determined (a) by precipitating a weighed amount of solution with acid, filtering on a Gooch crucible and drying at 105°; (b) by drying at 105° and subtracting the calculated weight of phosphate in the volume of solution used. The two values agreed satisfactorily. The value found for the partial specific volume at 19.6° was 0.761 but this is rather inaccurate owing to the dilute solution used.

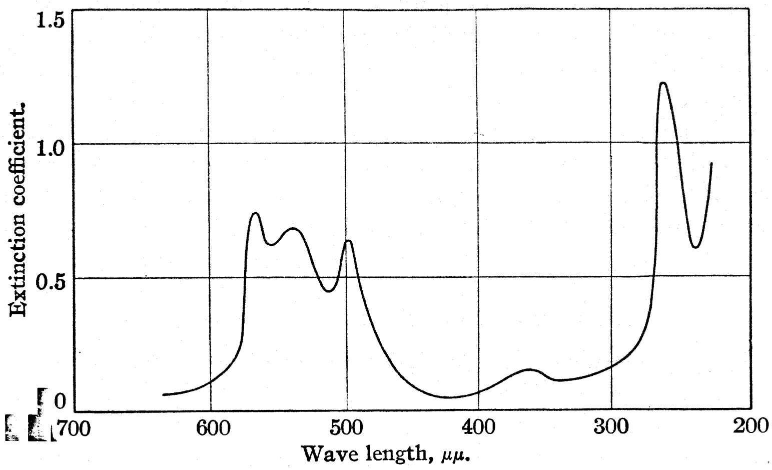

Fig. 1.—Light absorption for phycoerythrin (0.0097% solution).

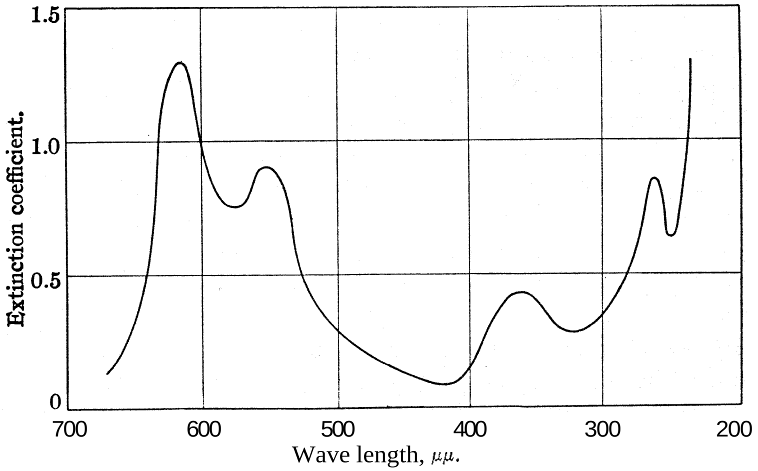

Fig. 2.—light absorption for phycocyan (0.0293% solution).

Light Absorption.—(In dilute phosphate buffer solution, PH = 6.8 and 7.0.) The absorption in the visible spectrum was measured with a Konig-Martens spectrophotometer and the results are given in Tables

I and II; for the ultraviolet a Judd-Lewis spectrophotometer was used; the values being of a lower order of accuracy they are not tabulated. The absorption curves obtained are shown in Figs. 1 and 2.

With phycoerythrin the absorption band in the visible was found to have three maxima, at 566, 540 and 497.5$\mu\mu$, agreeing with those obtained by Kylin[3] (569–565,541–537 and 498–492$\mu\mu$) and Kitasato[4] (562,526 and 495 $\mu\mu$, respectively). With phycocyan the maxima were found to be at 615 and 553$\mu\mu$, agreeing with those of Kylin (618–613 and 553–549$\mu\mu$, respectively) and Kitasato (614 and 546$\mu\mu$). In the ultraviolet both substances have bands with maxima at 262$\mu\mu$, and feebler, less well-defined ones at about 360$\mu\mu$ (Kitasato, approximately 270 and 330$\mu\mu$). With phycoerythrin the former band is much stronger than with phycocyan.

Determination of the Molecular Weight

A. By the Method of Sedimentation Equilibrium.—The apparatus and procedure have already been described.[5,6,7] With phycoerythrin photographs were taken in the visible spectrum (Wratten K3 filter), long-waved ultraviolet (Wratten or Corning nickel-glass filter), and short ultraviolet (quartz optical system, chlorine and bromine filters), the arrangements being as previously described.[5,6,7] In order to cut down the intensity of the mercury line 366$\mu\mu$ so as to get suitably long times of exposure, it was found convenient to insert a ground-glass screen between the mercury lamp and the water filter.

As standards, to correct for variation in intensity of the mercury lamp, solutions of potassium chromate of suitable strength were used, both for the long-waved and short-waved ultraviolet.

With phycocyan consistent results were not obtained with the short ultraviolet, possibly owing to a certain amount of decomposition during the run, so that the products formed would have absorption in the short ultraviolet, but not in the long ultraviolet or the visible, and hence the results would be affected only in experiments with the short ultraviolet. To increase the absorption in the long ultraviolet (since only a dilute solution of phycocyan was available), it was found necessary to use a cell of 8 mm. in thickness, as against 2 mm. in all other cases.

B. By the Method of Sedimentation Velocity.—The centrifuge and the method used have already been described.[8,9] Parallel light from the Pointolite lamp was used, with an Ilford three-color, green filter for phycoerythrin and a Lifa yellow filter for phycocyan. The plates used were Ilford

[5] Svedberg and Fåhraeus, THIS JOURNAL, 48, 430 (1926).

[6] Svedberg and Nichols, *ibid.*, 48, 3081 (1926).

[7] Svedberg, *Z. physik.* Chem., 121, 65 (1926).

[8] Svedberg, ibid., 127, 51 (1927).

[9] Svedberg and Nichols, THIS JOURNAL, 49, 2920 (1927).

Screened Chromatic, developed for from two to three minutes with metol developer.

Results

A. Sedimentation Equilibrium.—The formula for the molecular weight, M, is given[5] by

$$M = \frac{2RT \ln c_2/c_1}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where R is the gas constant, T the absolute temperature, V the partial specific volume of the protein, ρ the density of the solvent, c_2 and c_1 the

TABLE III

MOLECULAR WEIGHT OF PHYCOERYTHRIN

Concentration, 0.42 g. per 100 cc.; buffer solution PH = 6.8 (0.01 M in KH_2PO_4 and Na_2HPO_4); standard, K_2CrO_4, $M/1200$; filter, Wratten ultraviolet; plates, Hauff Extra Rapid. developed for two minutes in metol developer for soft effects; source of light, mercury arc with ground-glass screen; aperture of objective, $f/22.7$; times of exposure, 15, 30 and 60 seconds; exposures made after 44, 48 and 51 hours of centrifuging. $\omega = 188.7$~; $V = 0.748$; $\rho = 1.001$; $T = 290.4$; length of column of solution = 0.53 cm.; thickness of column = 0.200 cm.; b, the distance of the outer end of solution from axis of rotation = 4.73 cm.

Distances, cm.		Mean concn. (orig. soln. = 1.000)		No. of expt. used	Mol. wt., thousands
x_2	x_1	c_2	c_1		
4.65	4.60	1.57	1.277	3	227
4.60	4.55	1.277	1.056	12	212
4.55	4.50	1.056	0.889	15	214
4.50	4.45	0.889	.747	18	208
4.45	4.40	.747	.632	15	206
4.40	4.35	.632	.542	15	192
4.35	4.30	.542	.467	15	196
4.30	4.25	.467	.394	15	212
4.25	4.20	.394	.336	15	203
				Mean,	206,000

TABLE IV

MOLECULAR WEIGHT OF PHYCOCYAN

Concentration, 0.12 g. per 100 cc.; buffer solution, phosphate mixture, PH = 7.0; light source, Argenta lamp; filter, Wratten K3 (yellow); plates, Wellington Spectrum Panchromatic; development, 3 minutes in metol; aperture, $f/13.6$; times of exposure, 40, 60 and 90 secs.; exposures made after 40, 44 and 48 hours. $\omega = 239.7$~; $V\rho = 0.749$; length of column = 0.500 cm.; thickness of column = 0.200 cm.; $b = 4.73$ cm.; $T = 287°$.

Distances, cm.		Mean concn. (orig. soln. = 1.000)		No. of expt. used	Mol. wt., thousands
x_2	x_1	c_2	c_1		
4.63	4.58	1.258	1.088	11	105.5
4.58	4.53	1.088	0.953	11	97.6
4.53	4.48	0.953	.832	11	101.1
4.48	4.43	.832	.728	11	100.2
4.43	4.38	.728	.641	8	97.5
4.38	4.33	.641	.558	8	106.2
4.33	4.28	.558	.488	8	104.8
4.28	4.23	.488	.429	8	101.7
				Mean,	101,800

concentrations at distances x_2 and x_1, respectively, from the axis of rotation and ω the angular velocity.

The results of typical runs are given in Tables III and IV; the results for all the runs are summarized in Tables V and VI. It will be seen from Tables III and IV, and it was also the case in the other experiments, that there is no systematic variation in the values of the molecular weight with varying distance from the axis of rotation; in other words, the solutions consist of molecules of uniform size.

TABLE V

SUMMARY OF RESULTS FOR PHYCOERYTHRIN

Concn., g. per 100 cc.	PH	Absorption band used	Plates used	Filter used	Mol. wt.
0.081	6.8	Visible	Ilford iso zenith	Wratten K3	209,000
.042	6.8	Visible	Tlford iso zenith	Wratten K3	209,400
.42	5.0	Long ultra-violet	Hauff ultra rapid	Corning nickel glass	217,400
.42	6.8	Long ultra-violet	Hauff extra rapid	Wratten nickel glass	206,000
.21	6.8	Short ultra-violet	Wellington ordinary	Chlorine and bromine	201,500
.21	6.8	Short ultra-violet	Hauff ultra rapid	Chlorine and bromine	202,900
				Mean	207,700

TABLE VI

SUMMARY OF RESULTS FOR PHYCOCYAN

Concn., g. per 100 cc.	PH	Absorption band used	Plates used	Filter used	Mol. wt.
0.12	7.9	Visible	Wellington panchromatic	Wratten K3	112,600
.12	7.0	Visible	Wellington panchromatic	Wratten K3	101,800
.10	'7.0	Visible	Ilford screened chrom.	Wratten K3	114,400
..	6.8	Long ultra-violet	Hauff extra rapid	Wratten nickel glass	100,000
..	6.8	Long ultra-violet	Hauff extra rapid	Wratten nickel glass	100,600
				Mean	105,900

B. Sedimentation Velocity.—The molecular weight is given by[8]

$$M = \frac{RT}{D(1 - V\rho)} \cdot \frac{1}{\omega^2 x} \cdot \frac{dx}{dt} = \frac{RT}{D(1 - V\rho)} \cdot s$$

where s is the specific sedimentation velocity, D the diffusion constant, x the distance from the axis of rotation and the other symbols have the same meaning as before. D can be calculated from the amount of blurring of the boundary as previously described.[8,9] It must be pointed out that in these experiments, more particularly those with phycoerythrin, the values of D obtained are not very accurate, first, because the color-sensitized plates used do not appear to be as uniform, especially for **green** light, as the non-sensitized plates, thus making the determinations of concentration not so reliable; second, because with the relatively large sedimentation velocity and low diffusion constant, the time of centrifuging is shorter and thus the amount of diffusion much less; and third,

TABLE: VII

PHYCOERYTHRIN

Concentration = 0 084%; phosphate buffer, *P*H = 6.8; V = 0.755 at 30"; T = 303; length of column = 1 60 cm ; thickness of column = 0.20 cm.; exposure, 14 secs.; speed 39,050 r p.m. (1302π).

Time interval, min.	Δx per 20 min., *cm.*	Mean x, *cm.*	$\omega^2 x \times 10^{-7}$	*s*, cm./sec. $\times 10^{12}$	*D*, cm.^{2}/day
20– 40	0.129	4.55	7.60	1.40	0.057
40– 60	.141	4.68	7.82	1.46	.046
60– 80	.134	4.82	8.05	1.34	.053
80–100	.147	4.96	8.29	1.42	.051
100-120	.152	5.11	8.54	1.42	.051
120–140	.159	5.26	8.79	1.44	.063
			Mean	1.413	0.0535

Calculated molecular weight, 235,000.

TABLE VIII

PHYCOCYAN

Concn. = 0.1%; phosphate ***buffer,*** PH = 7.0; *V* = 0.755 at 30°; T = 303; length of column = 1.54 cm.; exposure = 15 sec.

Time interval, hours	*Ax* per half hour. cm.	Mean x, *cm.*	Speed, r.p.m.	$\omega^2 x \times 10^{-7}$	*s*, cm./sec. $\times 10^{13}$	D, cm.^{2}/day
$^1/_2$–1	0.090	4.56	39,100	7.64	6.42	(0.046)
1 –$1^1/_2$	.099	4.65	39,100	7.80	6.82	.0569
$1^1/_2$–2	.103	4.75	39,000	7.925	6.98	.0578
2 –$2^1/_2$	.106	4.85	39,000	8.105	6.98	.0626
$2^1/_2$–3	.109	4.97	39,000	8.29	7.01	.0617
3 –$3^1/_2$	.120	5.08	39,000	8.48	7.55	.0617
				Mean	6.96	0.0579

Calculated molecular weight, 107,000.

TABLE IX

Substance	*P*H	Mean speed. r.p.m.	T	D, cm.^{2}/day	s, cm./sec.	*M*
Phycoerythrin	5.0	38,900	303	0.0528	1.435×10^{-12}	242,000
Phycoerythrin	6.8	39,100	303	.0614	1.435	208,000
Phycoerythrin	6.8	39,050	303	.0535	1.413	235,000
Phycoerythrin	6.8	28,100	300	.0538	1.370×10^{-12}	222,000
Phycocyan	7.0	38,950	303	.0606	7.01×10^{-13}	103,000
Phycocyan	7.0	39,000	303	.0579	6.96	107,000
				Mean for phycoerythrin		227.000
				Mean for phycocyan		105,000

because the value of D depends on the square of this quantity, so that any error in the determination of the latter has a correspondingly larger effect. The value of s, on the other hand, can be determined with a much higher degree of accuracy.

Details of typical runs are given in Tables VII and VIII and they are summarized in Table IX.

Fig. 3 gives a reproduction of the photographs taken during the centrifuging of the phycoerythrin at 39,000 r.p.m., that is with a mean centrifugal force of 90,000 times that of gravity, and shows the condition of the solution at 20, 40, ... and 140 minutes after the start of the run; the top row is the scale of concentrations.

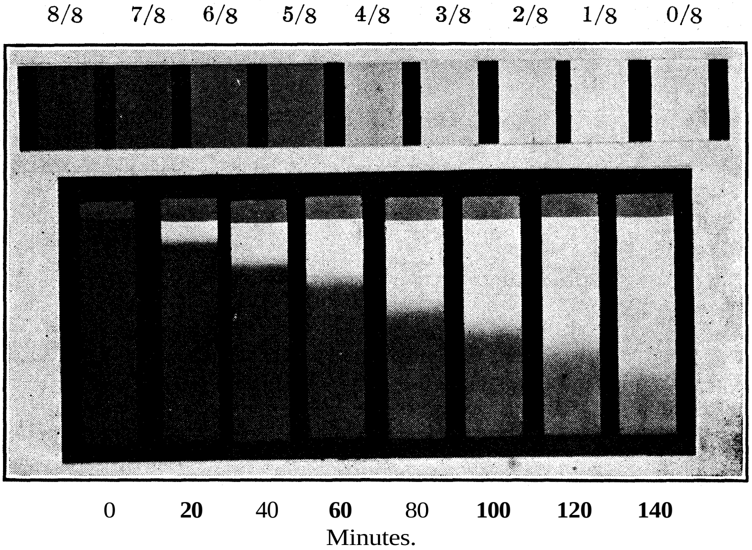

Fig. 3.

Fig. 4 shows the variation of concentration with distance after $^1/_2$, 1,. . . . . and $3^1/_2$ hours of centrifuging of phycocyan; the curves have been corrected for the decrease of concentration of the solution with time. The dotted curves for two and three hours represent the theoretical diffusion curves of a substance of only one molecular species. The deviation from the experimentally determined distribution is small and probably within the limits of experimental error. The same statement was also found to be true for the runs with phycoerythrin; that is, within the limits of experimental error, the molecules of both substances are uniform.

Examination of a Sample of Phycoerythrin Seventeen Years Old

A sample of Kylin's original phycoerythrin, which had also been prepared from *Ceramium rubrum*, was obtained through the courtesy of Professor Morner of the Biochemical Department. It had been kept for seventeen years in crystalline form under a saturated solution of ammonium sulfate covered with toluene.

Some of this substance was dialyzed for two weeks in a collodium bag against phosphate buffer solution ($P_H = 6.8$). The results of one run with this are shown in Fig. 5, which gives the variation of concentration with distance after 40, 65, 80 and 100 min. of centrifuging (speed 41,000–42,000 r. p. m.). The curves show marked divergences from those of a pure molecular species (see Fig. 4); Curve A shows the calculated curve for the pure substance after 80 minutes of centrifuging under the same conditions.

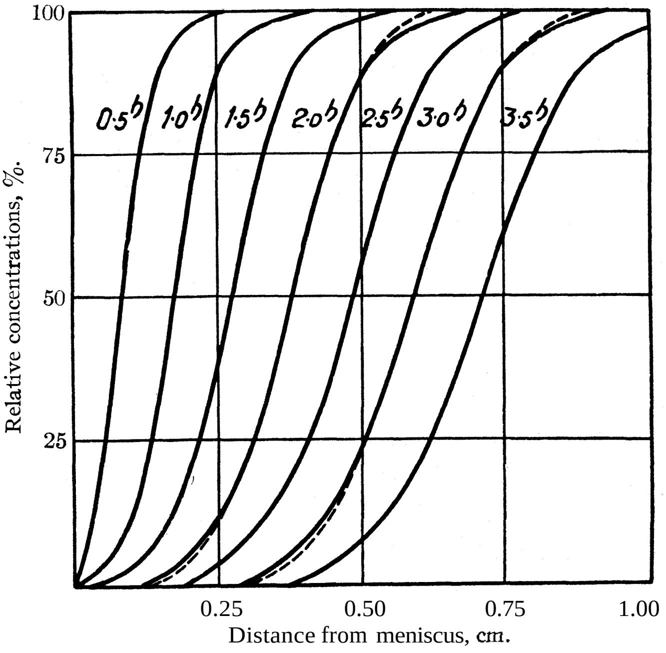

Fig. 4.

The curves show a point of inflection and evidently represent the distribution for a mixture of molecules of the normal size and of a smaller proportion of smaller ones so that the upper part corresponds to the distribution of the normal molecules and the lower to that of the smaller ones. From the amount of sedimentation corresponding to the lower part, it can be seen that these molecules were of $^1/_6$ or $^1/_8$ the weight of the normal ones. If we assume that the light absorption (in the green) per unit weight of these is the same as that for the normal molecules, an estimate can be made as to their proportion in the mixture. The values of s, the specific sedimentation velocity and of D, the diffusion constant for the normal molecules, were taken from the results of the previous experiments and were corrected for any difference of temperature from 30°; those of s and D for molecules of $^1/_6$ and $^1/_8$ the size were calculated (assuming spherical molecules and the validity of Einstein's law) and the theoretical distribution curves for various mixtures then obtained. The experimental accuracy is, however, not great enough to decide whether the smaller molecules are those of $^1/_6$ or $^1/_8$ the normal size. In Fig. 5 the dotted curves show the calculated distributions for a mixture of 70% of molecules of weight 208,000 and 30% of 208,000/8. A mixture of 67% of 208,000 and 33% of 208,000/6 was found to agree equally well with the experimental results. A second run at 41,000 r. p. m. gave similar results, as did also one at 28,000 r. p. m.

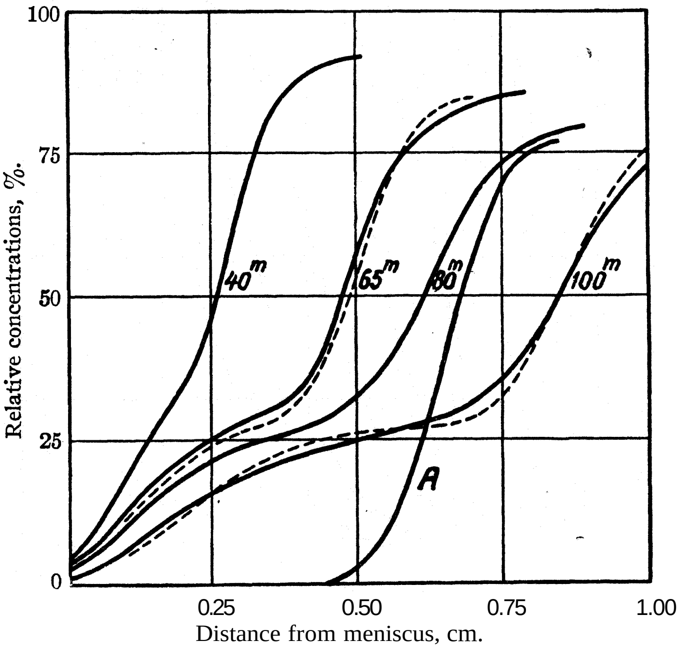

Fig. 5.

It was thought that the two kinds of molecules might be separable by recrystallization. Accordingly the material was recrystallized 6 times and the experiment repeated. The distribution curves still showed the presence of from 25 to 30% of the smaller molecules, so that very little, if any, separation had taken place.

Toward the end of the investigation the centrifuge was arranged so that photographs could be taken with short ultraviolet light. Under these conditions the recrystallized material gave qualitatively the same results as before, but the results were not suitable for quantitative information as to the composition of the mixture.

Discussion of Results

From the results it is considered that the most probable value of the molecular weight of phycoerythrin is 208,000 ± 8000 and of phycocyan 106,000 ± 5000, the former within the limits of experimental accuracy being double the latter. It is interesting to compare these values with those of the other two proteins already investigated in this Laboratory, namely, egg albumin and hemoglobin. We have for the molecular weight of egg albumin,[6] 34,500 ± 1000; for hemoglobin[10] it is 68,500 = 34,500 X 1.99; for phycocyan, = 34,500 × 3.07; and for phycoerythrin, = 34,500 X 6.03. The smaller molecules in the old sample of phycoerythrin may be of weight 208,000/6, that is, also approximating to 34,500.

The diffusion constant for phycoerythrin can be calculated from the Einstein formula

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi r\eta}$$

where R is the gas constant, N the number of molecules in one gram molecule, η the viscosity of the solution at temperature, T (for the dilute solutions used this was taken as the same as that for pure water, that is, 0.0080 gm. cm.$^{-1}$ sec.$^{-1}$ at 30°), r the radius of the molecule (assumed spherical); r is calculated from the molecular weight M by the formula $M/N = {}^4/_3\, \pi r^3 \rho$; ρ, the density, was assumed to be the reciprocal of the specific volume, the value being taken as 1.33. On this assumption $r = 3.95 \times 10^{-7}$ cm. The value of D calculated in this way is 0.061 cm.^{2}/day at 30°; experimental values were 0.061, 0.054 and 0.053, and the value obtained from the mean values of the molecular weight and specific sedimentation velocity was 0.061.

Thus the results agree very well with the assumption that the phycoerythrin molecule is spherical and has a density of 1.33. On the other hand, with phycocyan, which has practically the same diffusion constant and only half the molecular weight, the molecule must diverge widely from the spherical shape. Now Kitasato[4] found that these two substances had practically the same elementary composition, so that one could conclude that the phycoerythrin molecule is some sort of aggregation of two phycocyan molecules; or that it consists of an approximately spherical aggregation of smaller molecules and that phycocyan consists of an elongated-shaped aggregation of half the number of these smaller molecules.

Summary

1. The centrifugal sedimentation equilibrium and sedimentation velocity methods have been used to determine the molecular weights of phycoerythrin and phycocyan in dilute buffer solutions, using various

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[10] Mean of determinations by Svedberg, Fåhraeus and Nichols.

hydrogen-ion concentrations and protein concentrations, and using visible, long-waved ultraviolet and short-waved ultraviolet light.

2. Within the limits of experimental error none of these factors influenced the values found for the molecular weight, the value of phycoerythrin being 208,000 ± 8000, and for phycocyan 106,000 ± 5000.

3. Within the limits of experimental error both of these substances consisted of a pure molecular species.

4. A sample of phycoerythrin 17 years old was found to consist of molecules of weight 208,000, together with about 30% of molecules of $^1/_6$ or $^1/_8$ of this weight; no marked separation of the two sizes of molecule was effected by recrystallization.

5. It was pointed out that the molecular weights of phycoerythrin and phycocyan, as well as that of hemoglobin, approximately were multiples of that of egg albumin.

UPSALA, SWEDEN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY]

PURE ARSENOBENZENE AND THE MOLECULAR COMPLEXITY OF ARSENOBENZENE AND ARSENOMETHANE

BY CHARLES SHATTUCK PALMER AND ALBERT B. SCOTT[1]

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The structure of arseno compounds, which are probably the most important therapeutically and interesting chemically of all organic arsenicals, is not definitely known, although it has been quite generally accepted that they are analogous to the azo compounds, R—N=N—R. However, compounds of the two groups are quite different in solubility, ease of oxidation and reduction, action with chlorine and sulfur, etc. The published results on the molecular weights of symmetrical arseno compounds are conflicting and inadequate. The purpose of this investigation, therefore, was to determine the molecular weights of arseno compounds in associating and non-associating solvents in order to throw more light on the nature of their molecular structure.

Molecular weights for only three symmetrical compounds with the arseno linkage have been published. The first was for arsenomethane to which Auger,[2] in 1904, assigned the formula $(CH_3As)_4$ (I) from cryoscopic determinations on a solution of the yellow oil in benzene. But in 1926 Steinkopf, Schmidt and Smie[3] pointed out an error in his work and gave the

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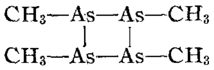
[1] Research Fellow under a grant from the Public Health Institute of Chicago. This paper is an abstract of a thesis presented by Albert B. Scott in partial fulfilment of the requirements for the degree of Master of Science at Northwestern University.

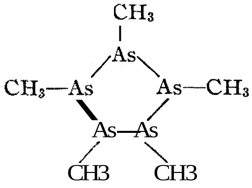
[2] Auger, Compt. *rend.,* 138, *1705 (1904).*

[3] Steinkopf, Schmidt and Smie, ***Ber.,*** 59, **1463 (1926).**

formula as $(CH_3As)_5$, which they represented structurally (II) as a cyclic compound with a ring of five arsenic atoms, never before known. The



I



II

molecular weight of arsenobenzene in benzene solution was determined by Michaelis and Schäfer[4] and a single value of 399.8 is reported. Although the calculated molecular weight for $C_6H_5—As{=}As—C_6H_5$ is 304, these authors state that their value proves that the molecule has the azo-type structure and that arsenobenzene is a true analog of azobenzene. The same investigators found widely divergent values for *p*-arsenotoluene.

Arsenomethane and arsenobenzene were chosen as the first compounds to be utilized in this investigation because the two values for the molecular weight of the former do not agree and the single value for the latter does not conform satisfactorily to the azo-type structure that it is supposed to demonstrate. Because of the ease with which arseno compounds are oxidized by air, special precautions, including the use of an inert atmosphere (carbon dioxide or nitrogen), are necessary in their preparation and in molecular weight determinations. For the latter, standard ebullioscopic and cryoscopic methods were used in this investigation and, as a check on their accuracy, compounds of known molecular weight were run under conditions the same as those used for the arseno compounds.

The method of Binz, Bauer and Hallstein[5] for the reduction of phenylarsonic acid to arsenobenzene by means of hypophosphorous acid was improved by changing the time and temperature of the reaction and introducing two alkali extractions and a final recrystallization; pure arseno benzene melting at 195° was thus obtained. Because of its slight solubility, the use of very dilute solutions was necessary in the molecular weight determinations, with some corresponding sacrifice of precision. By the ebullioscopic method in carbon disulfide and benzene mean values of 334 and 402, respectively, were obtained; while cryoscopic determinations in very dilute naphthalene solution gave an average value of 642. These results indicate the existence of the normal or azo-type structure, $C_6H_5—As{=}As—C_6H_5$, in a non-associating solvent (carbon disulfide), but distinct association in benzene (recognized as a common associating solvent) and especially in naphthalene, possibly with complete conversion into a double molecule in the latter solvent. The average value of 402

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[4] Michaelis and Schäfer, Ber., 46, 1742 (1913).

[5] Binz, Bauer and Hallstein, Ber., **53A,** 427 (1920).

in benzene solution confirms the work of Michaelis and Schäfer who found **309.8;** but their interpretation that arsenobenzene is normal in such a solution is probably wrong, since a mean value of 334, much nearer the theoretical, was found in carbon disulfide. The individual values obtained in naphthalene were widely divergent, due, probably, to the necessary use of an extremely dilute solution with consequent magnification of errors in thermal control. The mean value given was obtained after rejecting extremely high and extremely low values and may be regarded only as an indication of association.

Great care was necessary in the preparation of arsenomethane as the yellow oil because it is readily oxidized and also passes rapidly to red or brown-black, solid modifications of hitherto unknown molecular complexity. The preparation and molecular weight determinations were carried out in an inert atmosphere and the ebullioscopic solvents were saturated with nitrogen. The theoretical value of 450 suggested by Steinkopf, Schmidt and Smie for the molecular weight of the yellow oil was checked to within 5.3% by a mean value of 474 in carbon disulfide solution. A value of 476 (mean of two determinations giving 491 and 461) was found in benzene solution for the molecular weight of a mixture of about equal amounts of the red solid and yellow oil obtained by allowing the yellow oil to stand for four days in an inert atmosphere in a sealed ampule. The close agreement between the values obtained for the mixture and for the yellow oil alone makes it appear that the red solid has the same molecular weight, at least in solution, as the oil.

Experimental Part

Preparation of Arsenobenzene ($(C_6H_5—As=As—C_6H_5)_x$).—Analyses showed that the method of Binz, Bauer and Hallstein[5] for the reduction of phenylarsonic acid by hypophosphorous acid resulted in impure arsenobenzene. A satisfactory method of preparation was worked out as follows. A mixture of 1 liter of 50% hypophosphorous acid with a solution of 100 g. of recrystallized phenylarsonic acid[6] in 700 cc. of water was vigorously stirred in a flask fitted with a mercury-sealed stirrer in a water-bath at 55–60°. If a hard cake formed during the reaction it was pulverized in a mortar and returned to the flask. After four and one-half hours the reaction mixture was forced by carbon dioxide pressure into an anaerobic filter and the precipitate washed on the filter with 500 cc. of 10% sodium hydroxide solution followed by 500 cc. of warm 5% sodium hydroxide. During this filtration and during the entire subsequent purification process, all contact of the arseno compound with air was avoided by the maintenance of the compound or of the solution containing it in an atmosphere of carbon dioxide. The crude arsenobenzene was removed from the filter and vigorously stirred with two successive 200-cc. portions of 10% sodium hydroxide solution, the yellow powder being filtered off after each extraction and finally washed on the filter with 500 cc. of warm 5% sodium hydroxide followed by 1 liter of distilled water and dried for two days over phosphorus pentoxide in an evacuated carbon dioxide atmosphere. For **recrystallization,** the dry, crude product was dissolved in the minimum quantity of boiling chlorobenzene and the hot, filtered solution allowed to cool.

Palmer with Adams, THIS JOURNAL, 44,1361 (1922).

The first crop of crystals only was utilized. These were filtered off, washed with absolute ether, recrystallized as before and again washed with ether. The final product (weight about 12 g.) consisted of perfectly white needles melting at 195" when heated in the usual capillary tube at the rate of 1° per minute near the melting point. Other preparations described in the literature have melted at 196°,[7] 208°,[5] 212°.[4] Crystallographic examination of the arsenobenzene prepared in this investigation showed it to consist of strongly birefringent needles, all of one type.

Anal. Subs., 0.0995, 0.1051: 26.79 cc. iodine (a), 28.17 (b) [1 cc. (a) = 0.001839 g. As, (b) = 0.0018501. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: 49.51, 49.59.

Preparation of Arsenomethane $(CH_3As)_5$.—Following the general method of Auger,[2] arsenomethane was prepared as a bright yellow oil by stirring 100 g. of sodium methylarsonate with 350 cc. of 50% liypophosphorous acid for three hours in a water-bath at 70°. Traces of impurities in the sodium methylarsonate were found to cause immediate formation of brown and red solid modifications of arsenomethane, but the intermediate can be prepared in adequate purity by Quick and Adams'[8] modification of "Meyer's reaction," the product from the second recrystallization from alcohol being thoroughly washed with a mixture of equal volumes of alcohol and water to remove any trace of the original materials as well as all of the sodium iodide. The immiscible oil was transferred to a small separatory funnel, washed 5 times with 25-cc. portions of 5% sodium hydroxide solution followed by similar portions of water, and then sealed in ampules, all in an atmosphere of carbon dioxide; yield, good. The clear, yellow oil boiled at 178° under 15mm. pressure, but all attempts to purify it further by fractional distillation under reduced pressure resulted in the immediate formation of some of the red, solid modification, so the material was finally used without further purification.

Anal. Subs., 0.0553, 0.0563: 21.44, 21.48 cc. iodine (1 cc. = 0.002126 g. As). Calcd. for $(CH_3As)_5$: As, 83.30. (Auger found 82.50.) Found: 82.42, 81.11.

Molecular Weight Determinations.—In the ebullioscopic molecular weight determinations the apparatus and procedure of McCoy[9] were used. In the case of arsenomethane the solvents were previously saturated with nitrogen. In order to avoid undue dilution it was found desirable to dissolve the samples of arsenobenzene in the minimum amount of the desired solvent before the inner tube of the apparatus was placed in its final position. The usual apparatus and technique, with slow but continuous mechanical stirring, were employed for the cryoscopic determinations. As the temperature differences to be measured in the case of arsenobenzene are small, because of its slight solubility, particular care must be taken in thermal control. All temperatures were measured by an accurate Beckmann thermometer. Of the solvents used in the molecular weight determinations, the naphthalene was purified by two recrystallizations from alcohol followed by a fractional sublimation at about 70°; the benzene was the C. P., thiophene-free grade of the Eastman Kodak Company; and the carbon disulfide was obtained in exceptional purity by treating the technical product with ceresin wax according

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[7] Michaelis and Schulte, *Ber.*, 14, 912 (1881).

[8] Quick and Adams, THIS JOURNAL, 44, 809 (1922).

[9] McCoy, Am. Chem. J., 23, 353 (1900).

to the method of McKelvy and Simpson.[10] The data obtained for arsenobenzene and arsenomethane, together with those for standards run under the same conditions, are given in Tables I and II, respectively.

Table I

The Molecular Weight of Arsenobenzene in Various Solvents

A. Determinations in Naphthalene

Sample No.	Wt. of sample, g.	Wt. of solvent, g.	F. p. lowering, °C.	Mol. wt., found	Mol. wt., calcd.
p-Dibromobenzene Standards					
1	0.5327	9.996	1.584	232	
2	.1167	9.996	.351	229	$C_6H_4Br_2$
3	.3342	20.982	.482	228	236
			Mean =	230	
Arsenobenzene					
1	0.1813	10.113	0.181	684	
2	.0643	30.033	.025	591	
3	.1343	25.000	.060	618	$C_6H_5—As=As—C_6H_5$
4	.0709	25.000	.029	675	304
			Mean =	642	

B. Determinations in Benzene

Sample No.	wt. of sample, g.	Vol. of solvent, cc.	B. p. elevation, °C.	Mol. wt., found	Mol. wt., calcd.
Camphor Standards					
1	0.1310	31.70	0.100	136	$C_{10}H_{16}O$
	.0822	20.00	.090	150	152
			Mean =	143	
Arsenobenzene					
1	0.1184	18.00	0.051	423	
2	.1183	21.30	.050	364	$C_6H_5—As=As—C_6H_5$
3	.1661	26.00	.050	419	304
			Mean =	402	

C. Determinations in Carbon Disulfide

Sample No.	Wt. of sample, g.	Vol. of solvent, cc.	B. p. elevation, °C.	Mol. wt., found	Mol. wt., calcd.
p-Dibromobenzene Standards					
1	0.1220	17.00	0.057	244	
2	.1365	21.00	.050	252	$C_6H_4Br_2$
3	.2468	23.70	.088	230	236
			Mean =	242	
Arsenobenzene					
1	0.1487	17.00	0.050	339	
2	.1992	20.30	.058	328	$C_6H_5—As=As—C_6H_5$
3	.2025	18.00	.065	336	304
			Mean =	334	

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[10] McKelvy and Simpson, This Journal, 44, 108 (1922).

TABLE II

THE MOLECULAR WEIGHT OF THE RED AND YELLOW FORMS OF ARSENOMETHANE

Sample No.	Wt. of sample, g.	Vol. of solvent, cc.	B. p. elevation, °C.	Mol. wt., found	Mol. wt., calcd.
		p-Dibromobenzene Standards[a]			
1	0.7880	16.30	0.373	251	$C_6H_4Br_2$
2	.3643	28.50	.170	247	236
		A. Determinations on the yellow oil in carbon disulfide			
1	3.4825	16.00	0.875	483	
2	1.3533	16.00	.350	469	$(CH_3As)_5$
3	1.2029	15.00	.332	469	450
			Mean =	474	
		B. Determinations on a mixture of approximately equal amounts of the red and yellow forms of arsenomethane in benzene			
1	0.5988	32.00	0.125	491	$(CH_3As)_5$
2	.1756	25.00	.050	461	450
			Mean =	476	

[a] See Table I B and C for standards for Parts A and B of Table II. Additional *p*-dibromobenzene samples were run (1) in carbon disulfide saturated with nitrogen and (2) in benzene saturated with nitrogen.

Summary

1. A method for preparing pure arsenobenzene from phenylarsonic acid is given in detail.

2. Arsenobenzene has been found to have a molecular weight corresponding to the monomolecular, azo-type structure, $C_6H_5—As{=}As—C_6H_5$, in a non-associating solvent, but to be distinctly associated in benzene and naphthalene solutions.

3. $(CH_3As)_5$ and not $(CH_3As)_4$, the first formula suggested, has been confirmed as the molecular formula of arsenomethane in the form of the yellow oil, and the red, solid form may have the same molecular weight.

4. The custom of representing all arseno compounds by the general formula $R—As{=}As—R$ is unjustified.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF SODIUM-POTASSIUM ALLOY ON PETROLEUM[1]

BY J. B. CONANT[2] AND A. H. BLATT[3]

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When a sample of crude Pennsylvania petroleum, diluted with anhydrous ether, is shaken with sodium-potassium alloy in an inert atmosphere an intense brown solution and precipitate result. The color is discharged by introducing moisture or dry carbon dioxide. In the latter case large amounts of the gas are absorbed and a white precipitate is formed. This precipitate is evidently the sodium (or potassium) salt of an organic acid since it readily dissolves in water, and on acidifying the aqueous solution a solid organic acid is precipitated.

The behavior of the highly colored reaction mixture obtained by the action of the alloy on petroleum clearly indicates that an organo-sodium (or potassium) compound is present. Such a compound might be formed either by the cleavage of a highly substituted ethane[4] or by the addition of the metal to an unsaturated system.[5] The preliminary results which are reported below point to the latter alternative.

We have found that samples of a variety of crude oils (Mid-Continent, California and Colombia, S. A.) and a sample of "cracking-coil residue" from a Mid-Continent gas oil behave in a similar fashion when treated with sodium-potassium alloy. On the other hand, there was no reaction with a sample of "cracking-coil distillate" from Mid-Continent gas oil. Twelve to twenty-four hours of vigorous shaking appeared to complete the reaction as further treatment of the recovered oil gave no metallic derivative. We hope in a later investigation to isolate the highly colored metallic derivative and from it obtain the corresponding saturated hydrocarbon by treatment with moisture. For the present we have confined ourselves to a preliminary study of the acids which are produced by the action of carbon dioxide on the reaction mixture.

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[1] This paper contains preliminary results obtained in an investigation on "Isolation and Investigation of Thermo-Labile Hydrocarbons Present in Petroleum," listed as Project No. 16 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project 16.

[3] American Petroleum Institute Research Fellow.

[4] (a) Ziegler, *Ber.*, **56B,** 1743 (1923); (b) Conant and Garvey, THIS JOURNAL, 49, 2599 (1927).

[5] Schlenk, Ber., 47, 473 (1914).

The Preparation of Acids from Petroleum by the Action of the Alloy and Carbon Dioxide

After the petroleum-ether mixture had been shaken with sodium-potassium alloy for twenty-four hours, dry carbon dioxide was admitted. The gas was absorbed as the mixture was gently agitated and the brown color disappeared. During the absorption of the gas considerable heat was evolved. The excess alloy was decomposed with moist ether and alcohol and the mixture extracted with water. The aqueous layer was then acidified with hydrochloric acid,[6] which precipitated the organic acids as brown, amorphous powders. The details of a typical run are given in the experimental portion of this paper.

In order to determine how much, if any, "naphthenic acids"[7] were extracted from the petroleum by our treatment, we carried out a blank determination. A sample of the petroleum was shaken with alloy in the usual way. Then, instead of admitting carbon dioxide, moist ether was added. This lightened the color at once, presumably due to the decomposition of the metallic derivative by the water thus added. The reaction mixture, after decomposition of the excess alloy with alcohol, was extracted with water in exactly the same way as in the runs in which the acids were prepared. The aqueous solution was then acidified. In the case of the Pennsylvania and Colombia oils only the barest perceptible trace of precipitate was formed. In the case of the Mid-Continent cracking-coil residue a considerable amount of material was present at this point in the blank determination. This material was filtered, dried and weighed. It amounted to 2.5 g. per liter of oil. This is about 11% of the weight of the acid which was obtained when the reaction mixture from the same oil was treated with carbon dioxide.

These experiments, in which the reaction mixture was decomposed with moisture instead of carbon dioxide, serve to prove that the acids which we have prepared from the Pennsylvania and Colombia oils are practically free from naphthenic acids. In the case of the acids from the Mid-Continent cracking-coil residue, however, they were contaminated with about 11% of naphthenic acids. As we have no assurance that our method of purification would eliminate the naphthenic acids, we shall confine our attention in this paper to the acids prepared from the Pennsylvania and Colombia oils.

The crude acids are brown, amorphous solids without sharp melting points and may be mixtures of several compounds. They can be partially

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[6] It is of some interest that with California and Colombia oils, which are known to contain considerable sulfur, hydrogen sulfide was evolved on acidification of the aqueous layer. Apparently the alloy had removed at least a portion of the sulfur as metallic sulfides. This reaction may be of use in the study of the sulfur compounds of crude oils.

[7] We have used the term "naphthenic acids" to designate acidic material originally present in the oil and not formed by the action of alloy and carbon dioxide on the oil.

purified by solution in sodium carbonate, boiling the solution with decolorizing carbon and reprecipitation with hydrochloric acid. All attempts at further purification have so far failed. The acids could not be crystallized because in contact with organic solvents they formed thick oils. Distillation at 0.01 mm. was unsuccessful as the material decomposed before distilling. The substances contain no nitrogen, halogen or sulfur. (With the acids from the Colombia oil a faint sulfur test was obtained.) They are insoluble in boiling water and only slightly soluble in organic solvents. They dissolve in sodium hydroxide, sodium carbonate and sodium bicarbonate solutions. The samples for analysis were dried in a vacuum over phosphorus pentoxide.

TABLE I

Sample of oil	Condition of treatment	Yield,[a] g. per liter	Color	Melting point, °C.	Yield of "naphthenic acid" in blank run, g. per liter
Pennsylvania Crude[b]	Room temperature	10	Light tan	90–100, dec. at about 150	trace
Mid-Continent Crude[c]	Room temperature	5	Tan	120–130, dec. at about 170	1.2
Mid-Continent Cracking Coil Residue[c]	Room temperature	23	Dark brown	140–150, dec. at about 185	2.5
California Crude[c]	Room temperature	4.5	Light brown	125–130, dec. at about 150	.65
Colombia Crude[c]	Room temperature	17	Tan	110–120, dec. at about 140	trace

[a] Treated at room temperature.

[b] Kindly supplied by the Kendall Refining Company, Bradford, Pa. This oil is from the Bradford Field, near Bradford, Pa., and is obtained from a Devonian sand found at a depth of about 1500 feet.

[c] Kindly supplied by the Standard Oil Company of New Jersey. The cracking coil distillate and residue are from an oil which is a mixture of various Mid-Continent oils. The Mid-Continent Crude is also a composite sample. The California Crude is a so-called Southern California oil of gravity **26.3.** The Colombia Crude is a representative of the tank ship deliveries from Colombia, South America. It has the gravity **27.4.**

Table I summarizes the yield of acids obtained from different oils and the amount of naphthenic acids obtained in the blank determinations.

Analyses and Combining Weight

The acid from the crude Pennsylvania oil was studied in most detail. A number of samples prepared in different experiments were analyzed for carbon and hydrogen. The values for carbon varied between 75 and 77%. An average sample taken from a great many different runs, purified as carefully as possible and dried to constant weight in a vacuum, gave the following analysis which we consider the most significant: C, 76.0; H, 7.3. The combining weight was determined by titration in 50% alcohol solution with sodium hydroxide using a hydrogen electrode; the addition of the alcohol made the "break" somewhat sharper. The acid was dissolved in a known excess of standard alkali, half the volume of alcohol added, and titrated back with hydrochloric acid using the "break" of the titration curve, as determined by the hydrogen electrode, as the end-point. The combining weight thus found was 240 ± 10. The simplest empirical formula for the Pennsylvania acid from the analysis is C_6H_7O; this unit has the molecular weight of 95. Five times this unit would correspond to a dibasic acid with a molecular weight of 475 and a combining weight of 238. Thus the composition and combining weight correspond to an acid with the formula $(C_{28}H_{33}O)(COOH)_2$.

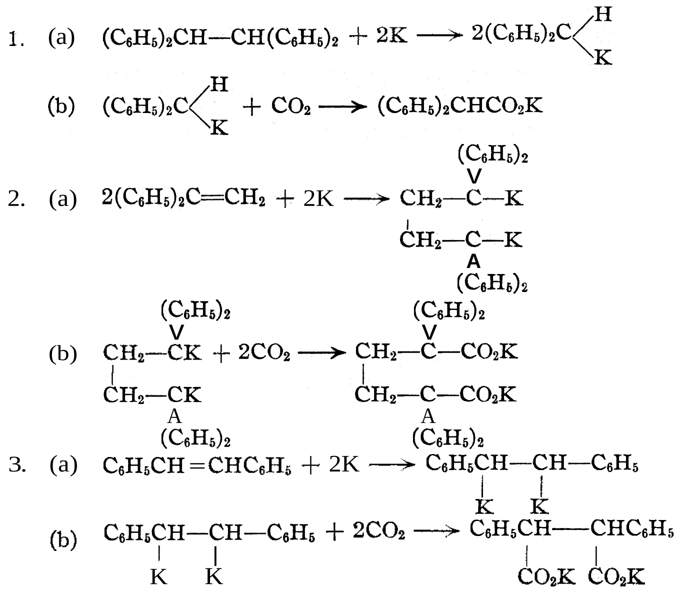
The composition of the Colombia acid was C, 75.8; H, = 8.0; its combining weight was 248. These numbers correspond to a unit $C_{6.3}H_8O$, with the molecular weight of 100. Five times this unit gives a dibasic acid $(C_{30}H_{38}O)(COOH)_2$, with the combining weight of 260.

Because of the insolubility of the acids in the usual solvents we have no direct determinations of their molecular weights. Indeed, considering the tendency of acids to associate in solution, significant molecular weight determinations could only be performed with some derivatives. Attempts to obtain solid esters have so far failed. On treating the Pennsylvania acid with thionyl chloride and then ammonia an amide was obtained as an amorphous solid. It was separated from any unchanged acid by extraction with sodium hydroxide, in which it was insoluble. It was insoluble in all the solvents tried and could not be further purified. The analysis points to an imide of a dibasic acid, but the results are far from conclusive. (Calcd. for $(C_{28}H_{33}O)(CO)_2NH$, N, 3.07. Calcd. for $C_{14}H_{36}CONH_2$, N, 6.0. Found: N, 4.54.)

While one cannot attach much significance to analytical data obtained with substances which are probably mixtures, one or two points are perhaps worthy of discussion. The formulas derived above are at best representative of the mean composition of the mixture. If the acids are mixtures of several isomeric substances, this representation may be very near the ultimate truth in regard to the composition of the components. It is evident that the substances are not aliphatic acids. An acid $C_nH_{2n+1}COOH$ with a combining weight of 256 is $C_{15}H_{31}COOH$. This has the composition C, 75.0; H, 12.5. Both the Pennsylvania acid (H, 7.3) and the Colombia acid (H, 8.0) contain far less hydrogen than an aliphatic acid. If we assume that the fifth atom of oxygen in our acids is a ketonic oxygen then the parent acid is $(C_{28}H_{35})(COOH)_2$ in the case of the Pennsylvania product, and $(C_{30}H_{40})(COOH)_2$ in the case of the Colombia product. These formulas are of the type $C_nH_{2n-21}(COOH)_2$ and $C_nH_{2n-20}(COOH)_2$, respectively. A dibasic acid with two phenyl groups, for example, diphenylsuccinic aid $(C_6H_5CH)_2(COOH)_2$ is of the type $C_nH_{2n-16}(COOH)_2$; with four phenyl groups $[(C_6H_5)_2C]_2(COOH)_2$, the type is $C_nH_{2n-32}(COOH)_2$. It will be evident from this that our acids contain less hydrogen than corresponds to one phenyl group per carboxyl and more hydrogen than corresponds to two phenyl groups per carboxyl. If the assumption were made that the extra atom of oxygen in our acids was linked as an ether, the type formulas would be for the Pennsylvania acid $C_nH_{2n-23}(COOH)_2$ and for the Colombia acid $C_nH_{2n-22}(COOH)_2$, and our tentative conclusion as to the degree of unsaturation of these acids would not be affected.

The inference that our acids contain at least one phenyl group per carboxyl group is substantiated by a consideration of the reactions in which organo-metallic derivatives, capable of yielding acids with carbon dioxide, are formed.[8]

These reactions are as follows



$$1.\ (a)\quad (C_6H_5)_2CH{-}CH(C_6H_5)_2 + 2K \longrightarrow 2(C_6H_5)_2C{<}^{H}_{K}$$

$$(b)\quad (C_6H_5)_2C{<}^{H}_{K} + CO_2 \longrightarrow (C_6H_5)_2CHCO_2K$$

$$2.\ (a)\quad 2(C_6H_5)_2C{=}CH_2 + 2K \longrightarrow \begin{array}{l} \qquad (C_6H_5)_2 \\ \qquad\ \ V \\ CH_2{-}C{-}K \\ | \\ CH_2{-}C{-}K \\ \qquad\ \ A \\ \qquad (C_6H_5)_2 \end{array}$$

$$(b)\quad \begin{array}{l} \quad (C_6H_5)_2 \\ \qquad V \\ CH_2{-}CK \\ | \\ CH_2{-}CK \\ \qquad A \\ \quad (C_6H_5)_2 \end{array} + 2CO_2 \longrightarrow \begin{array}{l} \quad (C_6H_5)_2 \\ \qquad V \\ CH_2{-}C{-}CO_2K \\ | \\ CH_2{-}C{-}CO_2K \\ \qquad A \\ \quad (C_6H_5)_2 \end{array}$$

$$3.\ (a)\quad C_6H_5CH{=}CHC_6H_5 + 2K \longrightarrow \begin{array}{l} C_6H_5\underset{K}{\underset{|}{CH}}{-}\underset{K}{\underset{|}{CH}}{-}C_6H_5 \end{array}$$

$$(b)\quad C_6H_5\underset{K}{\underset{|}{CH}}{-}\underset{K}{\underset{|}{CH}}{-}C_6H_5 + 2CO_2 \longrightarrow C_6H_5\underset{CO_2K}{\underset{|}{CH}}{-\!-}\underset{CO_2K}{\underset{|}{CH}}C_6H_5$$

It will be noted that all of these reactions give rise to phenylated acids. Reactions 1 and 2 yield acids with two phenyl groups per carboxyl group, while Reaction 3 yields acids containing one phenyl group per carboxyl group. In some work with synthetic hydrocarbons of known structure,[9] we have found that while Reaction 1 (cleavage) will not take place unless there are two phenyl groups on each carbon atom, Reaction 2 (dimolecular addition) will take place with compounds of the types $C_6H_5CH{=}CHR$ and $C_6H_5CH{=}CR_2$ (R = alkyl) and yields acids contain-

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[8] The possibility that the metallic derivatives were formed by the replacement of an active hydrogen atom by metal is removed by the fact that in none of our experiments was there any gas evolved. The amount of acid formed in a typical run of Pennsylvania oil would correspond to the liberation of about 50 cc. of hydrogen; in a typical run of Colombia oil to about 85 cc. of hydrogen. The gas volume in the reaction flask was about 100 cc. Consequently the increase in pressure due to the liberation of such volumes of hydrogen would be easily detected.

[9] Conant and Blatt, THIS JOURNAL 50, 551 (1928).

ing one phenyl group per carboxyl group. Therefore all of these possibilities must be reckoned with in the further study of this problem.

High Temperature Treatment of Pennsylvania Oil

The reaction with sodium-potassium alloy at low temperature in ether is complete in twelve hours, because further treatment failed to yield more material. Furthermore, at even 150° (in the absence of ether, of course) sodium-potassium alloy was without action on a sample of oil which had been put through the low temperature treatment.

Samples of the Pennsylvania oil which had been put through the low temperature treatment with sodium-potassium alloy were pumped free from ether and low-boiling constituents and treated with sodium-potassium alloy in the presence of carbon dioxide at 250". At this temperature two materials are formed, a dark brown, neutral substance insoluble in water and all organic solvents, and the sodium or potassium salt of some acid. The latter material was dissolved in water and the acid precipitated and dried in the same way as the acid from the low temperature runs. The yield in three hours was 10 g. of neutral material per liter of original oil and 3 g. of the acid material. The loss in volatilization during the pumping between the low temperature run and the high temperature run was 25 to 30% of the original oil.

The acid from the high temperature runs was a very dark, amorphous solid with the same intractable properties as the low temperature acids. A carefully purified sample was analyzed and the following numbers were obtained: C, 71.0; H, 5.9. A titration with the hydrogen electrode as the indicator showed a combining weight of 190. The analyses correspond to a unit $C_{4.1}H_{4.1}O$ with the weight of 69. The neutral material was insoluble in all solvents, except acetylene tetrabromide, in which it was slightly soluble on boiling. A certain amount of coloring material could be removed by boiling with ether. The material thus "purified" and dried was analyzed. It contained 15.6% of ash. The carbon and hydrogen analyses after correction for the ash were as follows: C, 85.6; H, 6.9.

It is impossible at present to suggest the nature of the reaction between the oil and the alloy at 250°. Not only may the reactions previously outlined be involved, but in addition dehydrogenation of alicyclic and saturated systems may take place.

Experimental Part

Treatment of Oils with Sodium-Potassium Alloy at Room Temperature

The general directions given for the Pennsylvania crude oil were followed in all the other cases. Consequently details will be given only when there was some variation in the procedure. In every case a sample of 100 cc. of oil, diluted with ether, was shaken first with a solution of sodium carbonate, then with 20% sodium hydroxide, and the alkaline extracts thus obtained were acidified. In no case was there evidence of more than traces of acids or phenols.

Low Temperature Treatment of Pennsylvania Crude with Alloy.[10]—Crude Pennsylvania petroleum was kept at room temperature under a vacuum of 15 mm. until no more

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[10] The alloy is prepared by melting together under xylene five parts of potassium and two parts of sodium. It is liquid above −10°.

gas was evolved. One hundred cc. of the petroleum thus treated was placed in a 250cc. distilling flask, then 6 cc. of alloy and 50 cc. of dry ether were added. The flask was stoppered, then alternately evacuated and filled with dry, purified nitrogen, through the side arm, five times. After the last filling with nitrogen the side arm of the flask was stoppered and the flask placed on a shaking machine. In the course of the first few minutes of shaking the reaction began and an intense, dark brown precipitate was formed. After twelve hours of shaking, the flask was repeatedly evacuated and filled with pure, dry carbon dioxide until no more was absorbed. The absorption of carbon dioxide was very vigorous and the contents of the flask warmed up almost to the boiling point of ether.

Ordinary ether was now added and the contents of the flask were transferred to a large beaker. The unused alloy was removed, and alcohol and finally water were added. The mixture of oil, ether, alcohol and water separated into layers. The water layer was removed and the ether layer extracted once with a dilute solution of sodium carbonate. The combined aqueous layers were extracted once with ether,[11] heated on the steam-bath to remove ether and alcohol, then boiled down to a small volume.

The resulting dark-brown, aqueous solution of the alkali salts was cooled and extracted twice with alcohol-free ether. The ether was removed from the water layer by an air blast and then the solution was acidified with dilute hydrochloric acid. The crude low-temperature acid was thus obtained as a brown, amorphous solid. It was filtered and dried. One gram of crude acid was obtained.

The acid was purified by solution in dilute sodium carbonate and repeated boiling with bone black. It was finally precipitated with hydrochloric acid, dissolved in dilute sodium hydroxide, filtered, precipitated with hydrochloric acid, filtered, washed with water, then dried. The dry powder was ground to insure homogeneity and dried to constant weight for analysis.

Anal. I. Subs., 0.1137: CO_2, 0.3173; H_2O, 0.0750. II. Subs., 0.1246: CO_2, 0.3472; H_2O, 0.0814. Found: I. C, 76.1; H, 7.4. II. C, 76.0; H, 7.3. Combining weight by titration in 50% alcohol: I. Subs.: 0.2983 g. required 5.99 cc. of 0.2 N NaOH. II. Subs.: 0.2983 g. required 6.37 cc. of 0.2 N NaOH. Found: I, 248; II, 234.

The purified acid softens on heating to 70–80°, and melts at about 100°. It is slightly soluble in the common organic solvents. Qualitative tests show the absence of nitrogen, sulfur and halogen.

When the acid is heated with thionyl chloride and the resulting acid chloride poured into ammonia, an imide is formed. The imide is insoluble in all the solvents tried. For analysis it was purified by extraction with dilute sodium hydroxide, then washed with water and dried.

Anal. Subs., 0.2504: 10.4 cc. of N_2, 28°, 761 mm. Found: N, 4.54.

Blank Run to Determine the Amount of Napthenic Acids Obtained from Crude Pennsylvania Oil.—One hundred cc. of oil was placed in a 250cc. distilling flask, then 6 cc. of alloy and 50 cc. of ether were added. The flask was filled with nitrogen, stoppered and shaken exactly as in the runs to prepare acid. After the shaking was completed the contents of the flask were poured onto moist ether, which discharged the color of the metallic derivative. The succeeding decomposition of excess alloy and extraction of the alkali salts were carried out exactly as in the carbon dioxide runs. On acidifying the alkaline aqueous solution there was only the barest preciptible precipitate.

Mid-Continent Crude Oil.—The yield of crude, dried acids from this oil was 0.5

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[11] The ether and the oil layers are combined and worked up to recover the oil. This process is described under the high temperature treatment.

g. per hundred cc. In the blank determination, decomposing with moist ether, the acid obtained from 100 cc. of oil amounted to 0.123 g.

The acids obtained by the carbon dioxide treatment were purified by solution in sodium carbonate, filtration to remove traces of non-acidic material and reprecipitation with hydrochloric acid. They were thus obtained as a brown, amorphous powder, free from nitrogen, halogen and sulfur, which, on heating, began to darken and shrivel at about 100°, melted at 120–130°, and decomposed with evolution of gas at about 170°.

Cracking Coil Distillate from Mid-Continent Oil.—This material gave practically no precipitate after shaking with alloy for twelve hours.

Cracking Coil Residue from Mid-Continent Oil.—This sample, a thick brown oil, gave the maximum yield of acids, 2.3 g. per 100 cc. of oil. In the blank determination 0.25 g. of naphthenic acids was obtained per 100 cc. of oil. The crude acids from the carbon dioxide runs were heated twice in carbonate solution with decolorizing carbon, the solution filtered, acidified and the precipitate filtered off and dried.

The purified acids thus obtained were chocolate brown in color and contained no sulfur, nitrogen or halogen. On heating they darkened at about 130°, melted at about 150" and some thirty degrees higher started to decompose with evolution of gas.

California Crude Oil.—On shaking with alloy the oil set to a stiff paste so that in each run it was necessary to use 100 cc. of ether for 100 cc. of oil. When the solution of the alkali salts of the acids was first acidified large amounts of hydrogen sulfide were evolved. The crude acids were purified by solution in alkali, filtration and precipitation with hydrochloric acid. The yield of crude, dry acid was 0.45 g. per 100 cc. of oil. In the blank run 0.065 g. of naphthenic acids per 100 cc. of oil was obtained.

Anal. Subs., 0.01326, 0.01411, 0.01498: CO_2, 0.03643, 0.03851, 0.04090; H_2O, 0.00826, 0.00871. Found: C, 74.95, 74.4, 74.5; H, 6.9, 6.7. Combining weight: Subs., 0.3100 g. required 6.89 cc. of 0.2 N NaOH. Found: 225.

The purified acids, light brown in color, contained neither nitrogen nor halogen. They gave a faint test for sulfur when fused with potassium and treated with sodium nitroprusside, but no color or precipitate with lead acetate. On heating to about 80" the acids began to shrivel and turn dark. At 125–130" they melted and at 140–150° decomposition with evolution of gas began.

Colombia Crude.—This oil, like the California crude, set to a paste on treatment with alloy so that it was necessary to use 100 cc. of ether with each 100 cc. of oil. On acidifying the alkaline solution of the acids for the first time there was much hydrogen sulfide evolved. The yield of crude acids in the carbon dioxide runs was 1.7 g. per 100 cc. of oil. In the blank determination, using the same volume of oil, only a bare trace of naphthenic acids was obtained. For purification the acids were treated in carbonate solution with decolorizing carbon, filtered, precipitated with hydrochloric acid, filtered and dried.

Anal. Subs., 0.1460, 0.1344, 0.1150: CO_2, 0.4068, 0.3730, 0.3175; H_2O, 0.0977, 0.0982, 0.0832. Found: C, 76.0, 75.9, 75.6; H, 7.5, 8.0, 8.0. Combining weight by titration in 50% alcohol: Subs., 0.2840 g. required 6.12 cc. of 0.2 N NaOH. Found: 232.

The acids contained neither nitrogen nor halogen. After fusion with potassium they gave a faint, positive test for sulfur with sodium nitroprusside, but no color or precipitate with lead acetate. They were light tan in color, amorphous and when heated began to shrivel and darken at about 75°. About 50° higher they melted, while at 140° decomposition, with evolution of gas, commenced.

High Temperature Treatment of Pennsylvania Oil with Alloy.—The mixture of oil, ether and alcohol recovered from the low temperature treatment was heated on the steam-bath, at ordinary pressure, then under a vacuum of 15 mm. to remove all low-boiling material and to dry the oil. One hundred cc. of the oil thus prepared, which did not differ in appearance from the crude oil, was placed in a 500cc. flask fitted with an inlet for pure, dry carbon dioxide, a stirrer with mercury seal, and a reflux condenser. Preliminary experiments showed that there was no reaction when the oil was heated to 150° in a current of carbon dioxide, and that there was a reaction at 250° with formation of neutral and acidic products. At 200° there is formation of acidic products but not of neutral products. We have worked at 250°.

The oil, 100 cc. with 10 cc. of alloy, was heated for three hours at 250° in a current of carbon dioxide, cooled, then worked up in a fashion similar to the low temperature runs, save that in the present case the insoluble product was separated by filtration.

The high temperature acid obtained in this fashion was a dark, almost black, amorphous solid. It was purified for analysis by reprecipitation, then dried. The purified material was very dark brown in color.

Anal. I. Subs., 0.2048: CO_2, 0.5336; H_2O, 0.1084. II. Subs., 0.2402: CO_2, 0.6260; H_2O, 0.1284. Found: I. C, 71.0; H, 5.9. II. C, 71.0; H, 5.9.

The acid was moderately soluble in acetone and alcohol, and slightly soluble in ether and benzene. On heating it decomposed at about 200°. Qualitative tests showed the absence of nitrogen, sulfur and halogens.

The neutral product was also dark brown in color. It was insoluble in all solvents tried, except in acetylene tetrabromide in which it dissolved to a small extent and separated as an oil on cooling. For purification it was boiled repeatedly with ether and dried. This material contained a large portion of ash, but no nitrogen or sulfur.

Anal. Ash: 0.1668 gave 0.0260 of non-combustible residue, or 15.6%. Subs., 0.1408 (corrected for ash): CO_2, 0.4419; H_2O, 0.0863. Found: C, 85.6; H, 6.9.

Summary

1. Samples of various crude petroleums and a cracking coil residue were treated with sodium-potassium alloy in dry ether in an atmosphere of nitrogen. Highly-colored metallic derivatives were formed which on treatment with carbon dioxide yielded alkali salts of organic acids. On acidifying the water solution of these salts, complicated mixtures of acids were precipitated.

2. The analysis of the mixed acids from the Pennsylvania and Colombia oils indicated that they contained one aromatic group per carboxyl group. They were free from nitrogen, halogens and sulfur.

3. A sample of the Pennsylvania oil which had reacted completely with the alloy at room temperature yielded alkali salts of acids when heated with the alloy and carbon dioxide at 250°. A considerable amount of amorphous, neutral material was also formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF SODIUM-POTASSIUM ALLOY ON CERTAIN HYDROCARBONS[1]

BY J. B. CONANT[2] AND A. H. BLATT[3]

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We have found that sodium-potassium alloy reacts with various samples of petroleum forming highly colored organometallic compounds. These on treatment with carbon dioxide yield the salts of a mixture of acids.[4] In order to throw more light on this interesting reaction we have studied the action of the alloy on certain pure hydrocarbons which have not been hitherto investigated from this standpoint. The analysis of the mixture of acids obtained from petroleum indicated the presence of one aryl group per carboxyl group. We have therefore turned our attention to two classes of hydrocarbons which might conceivably react with the alloy and carbon dioxide with the formation of acids similar to those obtained by us from petroleum.

Derivatives of Dibenzyl

The first class of substances prepared and investigated were derivatives of dibenzyl which may be represented by the general formula I. We prepared dimethyldiphenylethane ($R=CH_3$), di-isopropyldiphenylethane, ($R= (CH_3)_2CH-$), di-*n*-butyldiphenylethane ($R= C_4H_9$) and di-*tert.*-butyldiphenylethane ($R= (CH_3)_3C-$).

$$C_6H_5\underset{R}{CH}\underset{R}{CH}C_6H_5$$

I

Ziegler has shown[5] that tetraphenylethane ($R = C_6H_5$, Formula I) reacts with sodium-potassium alloy in ether forming the metallic derivative of diphenylmethane [$(C_6H_5)_2CHK$]. Dibenzyl itself does not undergo this reaction.[6] It was, therefore, a matter of considerable theoretical interest, quite aside from the petroleum problem, to see whether or not the derivatives containing alkyl groups would behave like dibenzyl or like tetraphenylethane,

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[1] This paper contains results obtained in an investigation on "Isolation and Investigation of Thermo-Labile Hydrocarbons Present in Petroleum" listed as Project 16 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project 16.

[3] American Petroleum Institute Research Fellow.

[4] Conant and Blatt, THIS JOURNAL, 50,542 (1928).

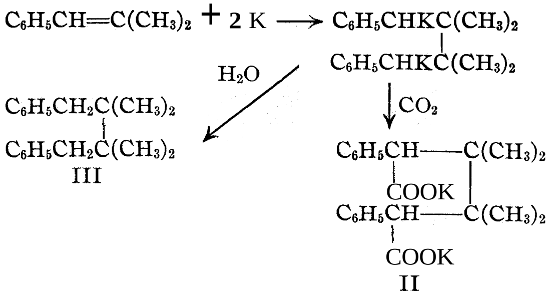
[5] Ziegler and Thielmann, *Ber.*, 56B, 1743 (1923).

[6] Conant and Garvey, THIS JOURNAL, 49,2599 (1927).

The results were all negative. After shaking the ethane with the alloy in ether in the usual way, more than 90% of the compound was recovered unchanged; there was no color produced and no evidence of a reaction. Even boiling the di-isopropyl and the di-*tert.*-butyl compounds, with the alloy in dioxane was without effect. It may be concluded, therefore, that the metallic compounds formed in the petroleum reaction were not produced as a result of the cleavage of di-aryl-di-alkyl ethanes. It is also evident that even the isopropyl and *tert.*-butyl groups are not equivalent to a phenyl group in increasing the reactivity of tetra-substituted ethanes toward sodium-potassium alloy. Considering the effectiveness of the branched alkyl groups in promoting dissociation in the dixanthyl series,? this is somewhat surprising. Since, however, even a tetra-aryl ethane reacts with sodium-potassium alloy and not with 40 per cent. sodium amalgam we are obviously dealing with about the limits of reactivity which can be estimated by the methods developed in this Laboratory.= Even if the dissociating influence of *sec.* and *tert.*-alkyl groups (as indicated by studies in the dixanthyl series)? is exerted in the tetra-substituted ethanes, a di-aryl di-*tert.*-alkyl ethane might just fall short of reacting with the alloy.

Derivatives of Styrene

Schlenk[8] has shown that unsymmetrical diphenylethylene $(C_6H_5)_2C{=}CH_2$ reacts with the alkali metals with the formation of the compound $(C_6H_5)_2CKCH_2CH_2CK(C_6H_5)_2$, (written as the potassium compound). A similar reaction has not been reported with unsaturated hydrocarbons containing one phenyl group, although Schlenk found that styrene $(C_6H_5CH{=}CH_2)$ reacts very slightly and then polymerizes. Using sodium-potassium alloy in ether we have found that propylstyrene $(C_6H_5CH{=}CHC_3H_6)$ and dimethylstyrene $(C_6H_5CH{=}C(CH_3)_2)$ yield metallic derivatives corresponding to the reaction characteristic of unsymmetrical diphenylethylene. On treatment with carbon dioxide, the salt of a dibasic acid is formed (II); with water a saturated hydrocarbon (III) is produced.



$$C_6H_5CH{=}C(CH_3)_2 + 2\,K \longrightarrow \begin{array}{c} C_6H_5CHKC(CH_3)_2 \\ | \\ C_6H_5CHKC(CH_3)_2 \end{array}$$

$$\begin{array}{c} C_6H_5CHKC(CH_3)_2 \\ | \\ C_6H_5CHKC(CH_3)_2 \end{array} \xrightarrow{H_2O} \begin{array}{c} C_6H_5CH_2C(CH_3)_2 \\ | \\ C_6H_5CH_2C(CH_3)_2 \end{array}\ \text{III}$$

$$\begin{array}{c} C_6H_5CHKC(CH_3)_2 \\ | \\ C_6H_5CHKC(CH_3)_2 \end{array} \xrightarrow{CO_2} \begin{array}{c} C_6H_5CH{-}C(CH_3)_2 \\ |\qquad\quad | \\ COOK\quad | \\ C_6H_5CH{-}C(CH_3)_2 \\ | \\ COOK \end{array}\ \text{II}$$

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[7] Conant, Small and Sloan, THIS JOURNAL, **48, 1743 (1926).**

[8] Schlenk, *et al., Ber.,* **47,473 (1914).**

The composition of the resulting acids, which have one phenyl group per carboxyl group, is similar to the composition of our petroleum acid. This reaction must, therefore, be considered among the possibilities. It might be noted in this connection that the color of the metallic derivatives is bright red while the compounds from petroleum are nearly black; the only dark metallic derivative that we have met in working with hydrocarbons of known structure is from stilbene. This is an indication (but not proof) that the organometallic compounds from petroleum are of the type

$$\text{Aryl-}\underset{\overset{|}{R}}{C}K\ \underset{\overset{|}{R}}{C}K\text{-aryl}$$

The hydrocarbon formed by the action of water on the reaction mixture from dimethylstyrene is tetramethyldibenzylethane (III above). It is a representative of a class of substances—the hexa-alkyl-ethanes—of which very few representatives are known. (The benzyl group is essentially a primary alkyl group.) We have been very anxious to prepare members of this class as we believe that if the alkyl groups are branched the hydrocarbons will be reactive and tend to disproportionate on heating. We are now investigating the action of the alloy on di-isopropylstyrene with the hope of preparing dibenzyl-tetra-isopropylethane.

Sodium potassium alloy is without action on di-benzyl-tetramethylethane (III) as would be expected since there are only primary groups attached to the ethane carbon atoms.

The results of the analyses of the hydrocarbons and certain of the acids were very irregular when the combustion was performed in the usual way. The percentages of both carbon and hydrogen were low. That the difficulty lay with the analysis and not with the purity of the compounds was shown by the irregularities with a given sample and by the fact that repeated crystallization from varied solvents was without effect. After repeated trials it was found possible to obtain results which were only 1 to 1.5% low in carbon. This was accomplished by burning the sample mixed with a large amount of copper oxide wire much as a Dumas nitrogen determination is carried out. In spite of these somewhat unsatisfactory analyses, the formulas of the compounds have been established without doubt. The hydrocarbons were shown to contain no nitrogen, sulfur or halogen and were not changed by boiling with zinc and acetic acid.. The molecular weights of all the substances were determined by the micro method using camphor. The formulas we have assigned are the only ones possible on the basis of these molecular weights and the analytical data. Our difficulties with the analyses seem to be connected with predominance of methyl groups in the compounds. It seems probable that methane (or formaldehyde) was formed in the combustion tube and escaped further oxidation.

Experimental

Preparation of the Carbinols

The phenyl alkyl carbinols were prepared by a uniform procedure. Benzaldehyde (in one case acetaldehyde) was added to an excess of the appropriate Grignard reagent, cold and free from excess magnesium. After standing overnight the reaction mixture was decomposed with ice and a slight excess of sulfuric acid, the ether layer separated and the aqueous layer extracted once with ether. The combined ether layers were washed with water, sodium carbonate, then water and dried over sodium sulfate. After removing the ether on the steam-bath, the residual material was distilled under reduced pressure. The yields given are based on the amount of aldehyde employed.

Phenylmethylcarbinol.[9]—Forty-four grams (1.0 mole) of acetaldehyde was added to the Grignard reagent (1.2 moles) prepared from 28.8 g. of magnesium, 190 g. of bromobenzene and 600 cc. of ether. The product boiled at 110–111° at 28 mm.; yield, 97 g. or 80%.

Phenyl*iso*propylcarbinol.[10]—Seventy-four grams (0.7 mole) of benzaldehyde was added to the reagent (1.0 mole) from 24 g. of magnesium, 130 g. of isopropyl bromide and 500 cc. of ether. The resulting carbinol boiled at 101–104° at 7 mm.; yield, 87 g. or 83%.

Phenylbutylcarbinol.[11]—Eighty-five grams (0.8 mole) of benzaldehyde was added to the reagent from 24 g. of magnesium, 100 g. of butyl chloride and 500 cc. of ether. The product boiled at 129–130° at 13 mm.; yield, 112 g. or 85%.

Phenyl-*tert*.-butylcarbinol.[12]—One hundred and twenty-seven grams (1.2 moles) of benzaldehyde was added to the reagent prepared from 72 g. of magnesium and 324 g. of *tert*.-butyl chloride and 1 liter of ether. On distillation the product boiled over a wide range but all the material which came over above 95° at 7 mm. solidified promptly in the receiving flasks. The yield was 118 g.; 60%. There was considerable residue which did not distil at a pressure of 7 mm. and bath temperature of 220°.

Preparation of the Bromides

The bromides were obtained by passing dry hydrogen bromide into the carbinols, which were kept cold by means of an ice-bath. Two layers soon formed: an upper one of organic bromide, a lower one of saturated aqueous hydrobromic acid. The reaction mixture was transferred to a separatory funnel, the lower layer drawn off, the organic bromide then placed in a beaker containing fused sodium sulfate and left in a desiccator over potassium hydroxide until free from hydrogen bromide. Finally, the product was distilled *in vacuo*.

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[9] Grignard, Ann. *chim.*, [7] 24, 466 (1901), from benzaldehyde and methylmagnesium iodide.

[10] Grignard, ref. 9, p. 467.

[11] (a) Puyal and Montagne, Bull. *soc. chim.*, [4] 27, 860 (1920); (b) Fourneau, Puyal and Montagne, *Anales soc. españ. fís. quím.*, 18,323 (1920); *C. A.*, 16,240 (1922).

[12] (a) Lepin, *J. Russ. Phys.-Chem. Soc.*, 44,1165 (1912); *Chem.* Centr., **1912,** II, 2080; (b) Ramart Lucas, *Compt.* rend., 150, 1061 (1910); (c) Ann. *chim.*, [8] 30, 361 (1913).

The purity of the bromides was controlled by Volhard analyses for bromine. A weighed sample of bromide was boiled for two hours with an excess of halogen-free sodium methylate then acidified with nitric acid. From this stage the regular Volhard procedure was followed.

All of the bromides were lachrymators.

Phenylmethylbromomethane.[13]—From 63 g. of carbinol there was obtained 70 g. of bromide, boiling at 92–94° under 8 mm.; yield, 74%.

Phenylisopropylbromomethane, $C_6H_5CHBrCH(CH_3)_2$.—Seventy-five grams of carbinol gave 68 g. of bromide, boiling at 116–119° at 17 mm.; yield, 64%. Calcd. for $C_{10}H_{13}Br$: Br, 37.6. Found: Br, 37.9.

Phenylbutylbromomethane, $C_6H_5CHBrC_4H_9$.—From 96 g. of phenylbutylcarbinol was obtained 96 g. of the bromide; boiling point 120–123° at 10 mm.; yield, 70%. Calcd. for $C_{11}H_{15}Br$: Br, 35.2. Found: Br, 34.2.

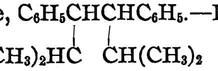
Phenyl-*tert*.-butylbromomethane.[12a]—From 65.6 g. of carbinol there was obtained 50 g. of the bromide, boiling point 106–112° at 9 mm.; yield, 55%.

Preparation of the Ethanes

The ethanes were prepared by adding a solution of the bromide in anhydrous ether (500 cc. ether per mole of bromide) to magnesium turnings, in the usual fashion of preparing a Grignard reagent. After the addition the solution was boiled for one and one-half hours, then cooled in an ice-bath while anhydrous cupric chloride (one mole per mole of bromide) was added. At this stage a vigorous reaction took place. The reaction mixture was left overnight, then decomposed with ice and hydrochloric acid, the ether layer separated, the aqueous layer extracted once with ether and the combined ether extracts were washed with water, carbonate solution, then water and dried over calcium chloride. On concentrating the ether the ethane was obtained.

Diphenyldimethylethane.[12a,13a]—From 74 g. of phenylmethylbromomethane, 9.6 g. of magnesium, 200 cc. of ether and 53 g. of anhydrous cupric chloride there was obtained 8.3 g. of ethane; yield, 20%. Considerable amounts of the oily isomer were formed at the same time. For use in the cleavage tests the ethane was crystallized four times from alcohol; m. p. 124–125'.

Diphenyl-di-isopropylethane,



$C_6H_5CH(CH(CH_3)_2)CH(CH(CH_3)_2)C_6H_5$

.—From 42.6 g. of phenyl-*iso*propylbromomethane, 4.8 g. magnesium, 100 cc. of ether and 27 g. of cupric chloride there was obtained 8 g. of the ethane; yield, 30%. The material is moderately soluble in cold ether and ethyl acetate, only slightly soluble in cold ethanol and acetic acid. It was purified by two crystallizations from glacial acetic acid, followed by a find crystallization from ethanol. From all of these solvents the ethane separates in very fine, white needles which melt at 150–150.5°.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.2; H, 9.8. Found: C, 88.1; H, 9.7.

Mol. wt.: subs., 0.0138: camphor, 0.1359; depression, 15.5°. K = 40,000. Calcd. for $C_{20}H_{26}$: mol. wt., 266. Pound: 262.

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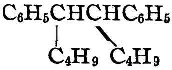
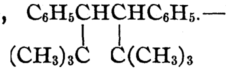
[13] (a) Radziszewski, *Ber.*, 7, 142 (1874); (b) Engler and Bethge, *Ber.*, 7, 1126 (1874).



Diphenyl-di-n-butylethane, $C_6H_5\underset{C_4H_9}{CH}\underset{C_4H_9}{CH}C_6H_5$.—Much difficulty was encountered in securing this ethane as a solid since small amounts of phenylamylene formed in the course of its preparation prevented crystallization. On evaporation of the ether after working up the reaction mixture an oil was invariably obtained. This was subjected to steam distillation, which removed the phenylamylene. The residue from the steam distillation when taken up in petroleum ether (2040°) and repeatedly evaporated gave a mushy solid mixed with oil. The solid and oil were separated by means of a sintered glass filter and the solid was then left on a porous plate. Finally it was crystallized from ethanol until it had a sharp and constant melting point at 80°. The yield of crude material dried on porous plate is small, about 10%. Once free from oil the ethane is only slightly soluble in alcohol, moderately soluble in ethyl acetate and quite soluble in ether.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.8; H, 10.2. Found: C, 88.4; H, 10.6.

Mol. wt.: subs., 0.0280; camphor, 0.2838; depression, 13°. Calcd. for $C_{22}H_{30}$: mol. wt., 294. Found: 305.



Diphenyl-di-*tert.*-butylethane, $C_6H_5\underset{(CH_3)_3C}{CH}\underset{C(CH_3)_3}{CH}C_6H_5$.—From 45.4 g. of phenyl-*tert.*-butylbromomethane, 4.8 g. of magnesium, 125 cc. of ether and 27 g. of cupric chloride there was obtained 7 g. of the ethane, a yield of 24%. The ethane is moderately soluble in ether, only slightly soluble cold in ethanol, acetic acid and ethyl acetate. For use in the cleavage tests it was twice crystallized from glacial acetic acid, then once from ethyl acetate: stout prisms, on very slow crystallization rectangular plates; m. p. 180–181°.

Anal. Calcd. for $C_{22}H_{30}$: C, 89.8; H, 10.2. Found: C, 88.7; H, 10.2.

Mol. wt.: subs., 0.0171; camphor, 0.1588; depression, 14°. Calcd. for $C_{22}H_{30}$: mol. wt., 294. Found: 308.

Treatment of the Ethanes with Alloy

In each experiment 0.0005 mole of purified ethane, 10 cc. of ether ("absolute" ether dried over phosphorus pentoxide, then sodium potassium alloy) and 1 cc. of alloy were sealed in glass tubes under nitrogen. After shaking for forty-eight hours and then standing for an additional 120 hours there was no evidence of reaction. The tubes were opened in an atmosphere of carbon dioxide, moist ether was added and the excess alloy removed. After the addition of water, the resulting ether layer and alkaline aqueous layer were worked up separately. In each case the ethane was recovered and its identity proved by a melting point and mixed melting point. With the dimethylethane 75% of the material was recovered, with the di-isopropylethane, 80%. In the cases of the di-*n*-butyl- and di-*tert.*-butylethanes, the recovery was over 90%. There were no acidic products formed.

Finally the di-isopropyl- and the di-*tert.*-butylethane were heated with alloy in dioxane at the boiling point of the solvent for ten minutes. No color developed and over 90% of the ethanes were recovered unchanged.

Action of Sodium-Potassium Alloy on Mono- and Di-alkyl Substituted Styrenes

a–Phenylamylene (7-Propylstyrene).[14]—The ethylene was prepared from phenylbutylbromomethane by boiling with sodium methylate solution. From 100 g. of crude bromide there was obtained 50 g. of α-phenylamylene, b. p. 212–215".

α,α′-Diphenyl-β,β′-dipropyladipic Acid.—When the alloy (5 cc.) is added to the phenylamylene (7.3 g.) there is no reaction. On addition of dry ether, 150 cc., there is immediate formation of a thin film of cherry-red metallic derivative over the surface of the alloy. The reaction mixture was sealed off under an atmosphere of purified nitrogen and shaken for twenty-four hours, then dry carbon dioxide admitted until the color of the metallic derivative disappeared.

Moist ether was next added and the excess of alloy removed. Finally water was added and the alkaline solution thus obtained was extracted twice with ether and heated on the steam-bath to remove dissolved ether. On cooling and acidifying with hydrochloric acid the organic acid separated as a white, slimy mass. It was dissolved in ether, the ether dried, concentrated and petroleum ether added. From this mixture the acid crystallized in small white cubes. These were purified by crystallization from alcohol. The melting point of the acid is 278°, uncorrected.

Anal. Calcd. for $C_{24}H_{30}O_4$: C, 75.4; H, 7.85. Found: C, 74.9; H, 8.0.

Phenyldimethylethylene and Alloy.—The ethylene was first prepared according to the procedure of Tiffeneau.[15] It is more convenient to heat the alcohol and oxalic acid in a flask fitted with a wide glass tube, 50 cm. long, at such a temperature that the water formed distils out of the top of the condenser. After the water has been removed, the temperature rises and anhydrous oxalic acid begins to sublime into the condenser. At this point the dehydration is complete.

α,α′ - Diphenyl - β,β,β′,β′ - tetramethyladipic Acid, $C_6H_5CH(COOH)C(CH_3)_2$-$C(CH_3)_2CH(COOH)C_6H_5$.—When the alloy (2 cc.) is added to 3.2 g. of the ethylene there is no reaction. Upon the addition of ether the formation of a cherry-red metallic derivative starts at once. The reaction mixture was shaken under nitrogen for thirty-six hours, then decomposed with dry carbon dioxide and worked up in the usual manner. From the alkaline layer over 2 g. of acid was obtained. The ether layer yielded a small amount of neutral material (see below—decomposition with water).

The acid was purified by crystallization from ether-petroleum ether, when it was obtained as white crystals melting at 238–240° with evolution of gas. For analysis it was vacuum dried at 80°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.6; H, 7.34. Found: C, 73.6; H, 7.5.

Mol. wt.: subs. 0.0101; camphor, 0.1113; depression, 10.5°. Calcd. for $C_{22}H_{26}O_4$: mol. wt., 354. Found: 346.

Dibenzyltetramethylethane, $C_6H_5CH_2C(CH_3)_2C(CH_3)_2CH_2C_6H_5$.—A mixture of 3.2 g. of ethylene, 3 cc. of alloy and 150 cc. of dry ether was shaken in an atmosphere of nitrogen for seventy-two hours, then decomposed with moist ether. On working up the ether layer there was obtained 2.2 g. of neutral material, identical with that found in small amounts in the carbon dioxide run. The neutral material was purified by crystallization from alcohol, from which it separated in fern-shaped aggregates of very fine, white needles, melting at 131–132°. For analysis it was dried in *vacuo* at 80°.

Anal. Calcd. for $C_{20}H_{26}$: C, 90.2; H, 9.8. Found: C, 89.0; H, 9.85.

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[14] (a) Schramm, *Ann.*, 218,392 (1883); (b) Klages, Ber., 39,2592 (1906).

[15] Tiffeneau, *Ann. chim.*, [8] 10, 365 (1907).

Mol. wt.: subs., 0.0090; camphor, 0.0893; depression, 15°. Calcd. for $C_{20}H_{26}$: mol. wt., 264. Found: 263.

Dibenzyltetramethylethane is very soluble in ether, moderately soluble in alcohol and ethyl acetate. It is unaffected by treatment with sodium-potassium alloy in dioxane at 100°. On heating 0.133 g. of the substance with alloy in dioxane at the boiling point for ten minutes no color was developed and on working up the products over 90% of the ethane was recovered unchanged.

Summary

1. Sodium-potassium alloy was found to be without action on diphenyldimethylethane, diphenyldibutylethane, diphenyl-di-isopropylethane and diphenyl-di-*tert.*-butylethane. The last three hydrocarbons are new.

2. Propylstyrene and dimethylstyrene add sodium and potassium alloy and undergo condensation. By the action of carbon dioxide derivatives of adipic acid were formed. The action of water on the metallic compound from dimethylstyrene yielded a hexa-alkyl ethane (dibenzyltetramethylethane).

CAMBRIDGE, MASSACHUSETTS

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

THE SYNTHESIS OF α,β,γ-TRIMETHYLGLUTARIC ACID

BY FRANCIS EARL RAY

RECEIVED NOVEMBER 7, 1927 PUBLISHED FEBRUARY 4, 1928

Introduction

In 1913 Noyes and Littleton[1] studied the decomposition of the methyl ester of *iso*-aminocamphonanic acid with nitrous acid. The only product isolated was the cis-camphonololactone. Later Noyes and Skinner[2] studied the same reaction and fractionated the decomposition products under reduced pressure. The fraction boiling at 86–88° (21 mm.) contained unsaturated acids. It was saponified and submitted to oxidation with alkaline permanganate, giving an acid which lost carbon dioxide at its melting point and supposedly formed α,β,β-trimethylglutaric acid.

Dr. Friedrich Richter in revising Beilstein's "Handbuch" found that α,β,β-trimethylglutaric acid had been previously obtained by Balbiano[3] and synthesized by Perkin and Thorpe[4] and kindly called Professor Noyes' attention to the oversight. The α,β,β-trimethylglutaric acid had a melting point of 88–89°. In view of this discrepancy, it seems evident that the acid melting at 111° obtained by Noyes and Skinner was not the α,β,β trimethylglutaric acid.

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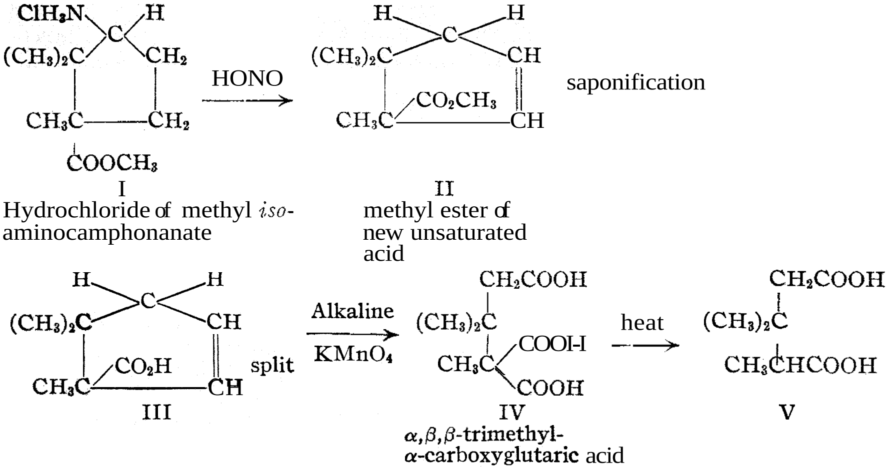
[1] Noyes and Littleton, THIS JOURNAL, 35, 75 (1913).

[2] Noyes and Skinner, *ibid.*, 39, 2692 (1917).

[3] Balbiano, *Ber.*, 27, 2136 (1894); 28, 1508 (1895).

[4] Perkin and Thorpe, J. *Chem.* SOC., 75, 65 (1899).

The formation and constitution of the compound obtained by Noyes and Skinner was explained by the following reactions



I Hydrochloride of methyl *iso*-aminocamphonanate

II methyl ester of new unsaturated acid

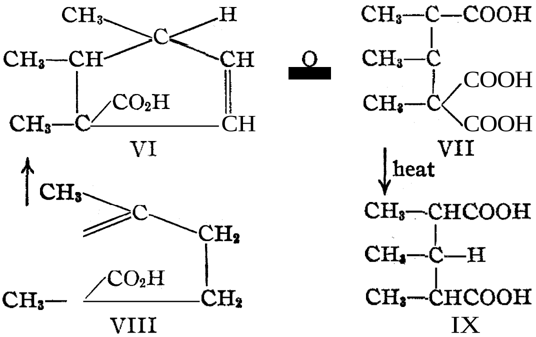
III

IV α,β,β-trimethyl-α-carboxyglutaric acid

V

Discussion

It was thought possible, therefore, that the reaction involved a rearrangement similar to the shift of the methyl group observed in the formation of lauronolic acid, which was also obtained in this decomposition and isolated in a higher-boiling fraction. If a migration of one of the gem methyl groups to the adjacent primary carbon atom occurs during the decomposition with nitrous acid, the compound VI might be formed. On this assumption oxidation would give α,β,γ-trimethyl-α-carboxyglutaric acid, VII, which would split off carbon dioxide and give α,β,γ-trimethylglutaric acid, IX. A shift of the double bond in lauronolic acid, VIII, might also give VI.



VI

VII

VIII Lauronolic acid

IX

A search of the literature failed to reveal the previous synthesis of α,β,γ-trimethylglutaric acid and its preparation was accordingly undertaken.

An attempt was made to prepare it by the Knoevenagel[5] reaction, which involved condensing 1 mole of acetaldehyde with 2 moles of malonic ester and then methylating the product in the a and γ positions. On hydrolysis with 1–1 hydrochloric acid, α,β,γ-trimethyl-α,γ-dicarboxyglutaric acid was obtained. This melted at 190° with decomposition. The liquid obtained by heating to split off carbon dioxide did not solidify and seemed by the wide range of its boiling point to be a mixture.

Other condensations tried were acetaldehyde and cyano-acetic ester, acetaldehyde and aceto-acetic ester, ethylidene chloride and cyanoacetic ester and ethylidene malonic ester and malonic ester. From all of these the tetracarboxylic acid was obtained but on decomposition the desired glutaric acid could not be isolated.

It was thought that the symmetrical character of the molecule militated against its successful decomposition. Accordingly, the attempt was made to prepare a derivative of an unsymmetrical nature. It might be supposed that such an acid would melt (with evolution of carbon dioxide) at a lower temperature than the tetracarboxylic acid and so avoid the profound change that seemed to take place when an attempt was made to split off carbon dioxide from the tetrabasic acid.

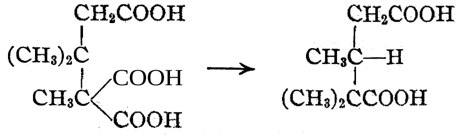
The synthesis adopted was as follows: ethylmethylacetic acid was prepared from malonic ester in the usual manner. This was brominated, and esterified and then unsaturated by boiling with quinoline. Cyanoacetic or malonic ester was condensed with this unsaturated ester by means of sodium ethylate. The product so obtained was methylated and hydrolyzed by prolonged boiling with potash. The α,β,γ-trimethyl-a-carboxyglutaric acid so obtained melted with evolution of carbon dioxide at 144° and the α,β,γ-trimethylglutaric acid, after repeated recrystallization, melted at 134°. A mixed melting point determination with Dr. Skinner's acid melted at 95–100".

It seems, therefore, that the acid obtained by Noyes and Skinner was not α,β,γ-trimethylglutaric acid.

Dr. Richter has also called attention to an α,α,β-trimethylglutaric acid prepared by Perkin and Thorpe,[6] which has a melting point of 112°. The supposed α,β,β acid of Noyes and Skinner melted at 111°. The similarity of melting points suggested the preparation of the α,α,β compound. The acid obtained was not fully purified but on comparison with the compound supplied by Dr. Skinner by a mixed melting point, the two were found to be identical. Dr. Skinner in a private communication has expressed the opinion that during the decomposition of the α,β,β-trimethyl-a-carboxyglutaric acid, one of the β methyl groups migrates to the a position, forming α,α,β-trimethylglutaric acid.

[5] Knoevenagel, Ber., 27, 2345 (1894); Ann., 281, 104 (1894).

[6] Perkin and Thorpe, J. Chem. *Soc.*, 71, 1185 (1897).



X XI

Experimental Part

Ethylidene **Dimalonic** Ester.—One hundred and sixty g. of malonic ester and 22 g. of acetaldehyde, both freshly distilled, were mixed and cooled to 0°. Five g. of **diethylamine** was added slowly with stirring and the mixture allowed to stand overnight. It was heated for five to six hours and then twice distilled; b. p. 200–210° (20 mm.), 170-175" (1 mm.), yield 18–20 g.

α,β,γ-Trimethyl-α,γ-dicarboxyglutaric Ester.—The above-mentioned product was added to 2.6 g. of sodium dissolved in 28 cc. of absolute alcohol and then treated with 16 g. of methyl iodide. After heating for three to four hours on the water-bath the alcohol was distilled off and the ester extracted and distilled; b. p. 190–195° (2–3 mm.), yield about 5 g. Considerable tar always remained in the flask after the distillation.

α,β,γ-Trimethyl-α,γ-dicarboxyglutaric Acid.—Five g. of the ester was boiled over the free flame with 25 cc. of 1–1 hydrochloric acid for twenty-four hours. The tar was removed by filtration and the filtrate on concentration deposited the crystalline acid. After one recrystallization from alcohol it melted sharply at 190°.

Anal. Subs., 0.0414: 6.34 cc. of 0.1 *N* alkali. Calcd. for $C_{10}H_{14}O_8$: 6.34 cc. Subs., 0.0933: CO_2, 0.1585; H_2O, 0.0541. Calcd. for $C_{10}H_{14}O_8$: H, 5.38; C, 45.79. Found: H, 5.4; C, 46.3.

0.8662 g. of this tetracarboxylic acid was heated to 190–200° and the products were aspirated through calcium chloride and soda lime. After twenty-five minutes the weight of the carbon dioxide bulb became constant and showed a gain of 0.2750 g. or 31.75%; theoretical, 33.6%.

The liquid residue was boiled with a few drops of 1–1 hydrochloric acid to destroy any anhydride formed but no crystals were obtained on evaporation of the ether extract. On distillation the product boiled over a range of 142–180°. It was evidently a mixture of various products.

Bromo-ethylmethylacetic Acid.—Ethylmethylacetic acid was prepared from malonic ester in the usual manner. Fifty g. was obtained. One hundred and twenty g. of phosphorus pentachloride and 80 g. of bromine were used to brominate the acid. It was then esterified, washed and distilled. Ninety g. boiling at 75–80" (25 mm.) was obtained.

Tiglic Ester.—The bromo ester was boiled with 65 g. of quinoline for two hours and allowed to stand overnight. The unsaturated tiglic ester was decanted and distilled; yield, 35 g. boiling at 100° (30 mm.).

Condensation of Tiglic Ester **and Cyano-acetic** Ester.—Ten g. of tiglic ester and 15 g. of cyano-acetic ester were boiled with 0.25 g. of sodium in 4 cc. of absolute alcohol for eight hours. The mass was then poured into ice-cold, acidulated water, extracted, dried and distilled; yield 8 g. boiling at 150–170° (30 mm.).

Methylation of **β,γ-Dimethyl-α-cyanoglutaric** Ester.—This product was methylated by 0.7 g. of sodium dissolved in 15 cc. of absolute alcohol and 5 g. of methyl iodide. After extraction and distillation 6 g. of α,β,γ-trimethyl-α-cyanoglutaric ester was obtained boiling at 140–150° (1–2 mm.).

α,β,γ-Trimethyl-α-carboxyglutaric Acid.—The ester was hydrolyzed with 10 g. of potash dissolved in 10 cc. of water. It was heated on the water-bath and the evolved ammonia collected in acid. After forty-eight hours only about 50% of the theoretical amount of ammonia had been evolved. It was then boiled over a small flame for sixteen hours until over 90% of the calculated ammonia had been collected and no further appreciable amount was given off. Two methods of isolating the free acid were used with about equal success. The first consisted in acidifying and extracting with ether and the second in preparing the barium salt by adding a concentrated solution of barium chloride to the alkaline solution of the acid. The barium salt, which is less soluble in hot than in cold solution, was washed with hot water, acidified with hydrochloric acid, dried and extracted with alcohol. The extracts from both procedures on spontaneous evaporation were clear, colorless sirups which crystallized after standing for several days. It was difficult to find a suitable solvent for recrystallization, After many experiments a mixture of benzene and acetone was used. It was generally necessary to allow the solution to stand overnight before crystals were deposited. After several recrystallizations the acid melted at 144–145° with decomposition.

Anal. Subs., 0.0063: Ag, 0.0038. Calcd. for silver salt: 60.1. Found: 60.3. Subs., 0.0222: 2.55 cc. of 0.1 N alkali. Calcd. for $C_8H_{14}O_4$: 2.54.

α,β,γ-Trimethylglutaric Acid.—The a-carboxy acid, in a test-tube immersed in an oil-bath, was heated at 150–160° for twenty minutes to split off carbon dioxide. On cooling the mass solidified and after ten recrystallizations from benzene the melting point was raised from 107 to 134°.

Condensation of Tiglic Ester with **Malonic** Ester.—In a manner precisely similar to the foregoing 20 g. of tiglic ester was condensed with 30 g. of malonic ester and the product methylated; boiling point 181° (25 mm.).

Anal. Subs., 0.1093: H_2O, 0.0870; CO_2, 0.2412. Calcd. for $C_{15}H_{26}O_6$: H, 8.61; C, 60.0. Found: H, 8.83; C, 60.1.

The ester was hydrolyzed with concentrated potash but the acid did not crystallize. It was distilled to split off carbon dioxide and the anhydride so formed was hydrolyzed by warming with a few drops of dilute hydrochloric acid. On evaporation α,β,γ-trimethylglutaric acid melting at 134° was obtained.

α,α,β-Trimethylglutaric Acid.—This acid was prepared according to the methods given by Perkin and Thorpe.[4] The acid after twelve recrystallizations melted at 103–104°. Lack of material prevented its further purification. A mixture of approximately equal amounts of this α,α,β-trimethylglutaric acid and of Dr. Skinner's acid melted at 105°.

Conclusion

It seems probable that α,α,β-trimethylglutaric acid is formed from α,β,β-trimethyl-α-carboxyglutaric acid by a shift of one of the 8-methyl groups to the α position upon loss of carbon dioxide, as Dr. Skinner suggests.

The writer wishes to express his sincere appreciation to Professor W. A. Noyes for the help and encouragement received during the progress of this investigation which was conducted in the latter's laboratory at Urbana, Illinois.

Summary

The decomposition of the methyl ester of *iso*-aminocamphonanic acid with nitrous acid gives a fraction boiling at 86–88' (21 mm.), which consists of unsaturated acids. On saponification and oxidation of this ma-

terial with alkaline permanganate and loss of carbon dioxide an acid was obtained by Noyes and Skinner which was thought to be α,β,β-trimethylglutaric acid.

The possibility of this acid being α,β,γ-trimethylglutaric acid has been eliminated by the synthesis of this compound and direct comparison with a sample of the original acid. The α,β,γ- is a new acid and completes the trimethylglutaric acid series.

It has been shown also that the compound obtained by Noyes and Skinner is α,α,β-trimethylglutaric acid.

GRINNELL, IOWA

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

LOCAL ANESTHETICS DERIVED FROM JL-PIPERIDYL CARBINOL

BY L. T. SANDBORN[1] WITH C. S. MARVEL

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Some of the molecular structures which produce local anesthetic action are very well known. Numerous compounds have been prepared in the attempt to find the best combination of high anesthetic value and low toxicity which is desirable for this type of drug. The earlier synthetic substitutes for cocaine were usually esters of cyclic amino alcohols; then with the discovery of novocaine the esters of open chain amino alcohols became more important. Recently McElvain[2] has shown that in a series with very closely related structures the closed ring derivatives are much more efficient in anesthetic action.

In connection with some other researches, a method for the preparation of 8-piperidyl carbinol (II) was developed. The fact that it was a cyclic amino alcohol at once suggested its use for the synthesis of a compound which should have local anesthetic action. The very favorable properties which were shown by this substance led to a more complete study of the derivatives of β-piperidyl carbinol with a view to producing a drug that might have properties better than any of those now available. @-Piperidyl carbinol was obtained in about 43% yields by the reduction of ethyl nicotinate (I) with sodium and absolute alcohol. It was also obtained in 50% yields by a similar reduction of ethyl nipecotate, but the difficulties involved in the preparation of nipecotic ester make the former method more practical. It has the properties that would be expected of an amino alcohol of this type.

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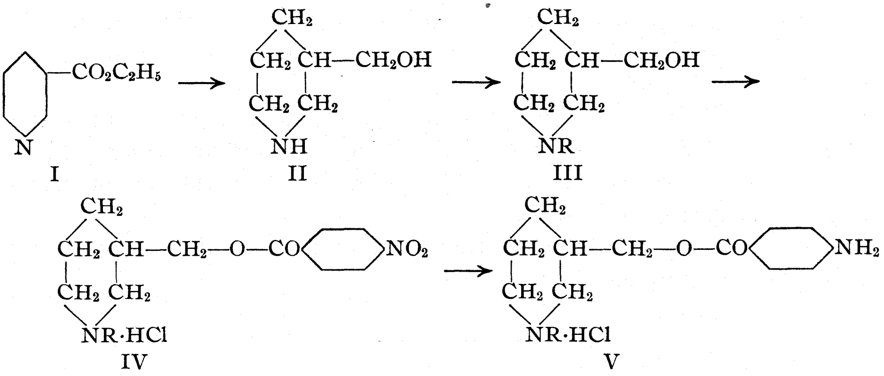
[1] This communication is an abstract of a thesis submitted by L. T. Sandborn in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] McElvain, THIS JOURNAL, 46, 1721 (1924).



The common local anesthetics are p-aminobenzoates of tertiary amino alcohols. 0-Piperidyl carbinol (a secondary amino alcohol) was therefore first alkylated on the nitrogen by treatment with an alkyl halide. The N-alkyl derivatives (III) obtained were the methyl, ethyl, isopropyl, *n*-butyl and allyl compounds. All of the alkyl derivatives boiled very close to the original carbinol and there was some difficulty on this account in obtaining them in a pure condition. The scheme finally adopted for their purification was to titrate the mixture of alkylated and unalkylated carbinol with standard acid and to obtain a mean molecular weight. From this value the amount of unalkylated carbinol was calculated. Then enough benzoyl chloride was added to react with the secondary amine to form the benzoyl amide. The alkylated carbinol was then extracted from this mixture with dilute acid, reprecipitated with alkali and extracted with benzene. An attempt was made to purify the carbinols by converting them to the hydrochlorides and crystallizing these derivatives. The salts were too hygroscopic for easy crystallization.

The N-alkyl-0-piperidyl carbinols were converted to the *p*-nitrobenzoyl ester hydrochlorides (IV) by the action of p-nitrobenzoyl chloride. The nitro ester hydrochlorides were reduced to the corresponding amino ester hydrochlorides (V) with hydrogen in the presence of a platinum-oxide platinum black catalyst.[3] This process could not be used on the allyl derivative and reduction with iron and hydrochloric acid was tried. The reduced product was not isolated in a crystalline condition either as a free base or as a salt.

Pharmacological Tests[4]

A 1% solution of the monohydrochloride of each amino ester was used. The toxicity was determined by intravenous injection in rabbits and the

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[3] Adams and Shriner, THIS JOURNAL, 45,2171 (1923).

[4] The pharmacological tests were performed by H. J. Cannon at the Abbott Laboratories. The authors desire to take this opportunity of expressing their thanks to the Abbott Laboratories for their kind assistance in this investigation.

onset time and duration of anesthesia by application to the cornea of a rabbit's eye.

TABLE: I

PHARMACOLOGICAL PROPERTIES

Alkyl carbinol	Average onset time in min.	Average duration of anesthesia in minutes	Minimum lethal dose in mg. per kg. of body weight
Methyl	2	25	15
Ethyl	1.5	4,550	16
Isopropyl	3.5–3.75	30–35	16
n-Butyl	1.75	25-30	15

These pharmacological properties compare very favorably with those of the local anesthetics now in common use.

Experimental Part

β-Piperidyl Carbinol.—In a 5-liter two-necked, round-bottomed flask fitted with a large bore condenser and a mechanical stirrer, was placed 800 cc. of absolute alcohol (dried with sodium or magnesium methylate) and 45.3 g. (0.3 mole) of ethyl nicotinate. The solution was stirred and heated to boiling over a flame. The flame was then removed and 92 g. (4 atoms) of sodium was added through the condenser as rapidly as possible.

In our experiments several rather characteristic color changes were noticed during the reduction. A green color appeared when the first portion of sodium was added. This color then quickly disappeared and the mixture turned yellow. At this point moderate foaming occurred. As the reaction continued, there was a gradual change in color from yellow to reddish brown and then back to light yellow. With this last change the sodium, which was usually in fairly large pieces up to this stage, melted and was broken up into fine globules which were suspended in the alcohol. A vigorous reaction set in, foaming occurred and it was often necessary to cool the flask with wet towels to prevent loss of material through the condenser. On the other hand, if this vigorous reaction did not set in by the time all of the sodium had been added, the flask was heated until it did occur. Occasionally it was necessary to add a 100-cc. portion of absolute alcohol to keep the sodium ethylate in solution.

The reaction mixture was heated for about a half hour after the sodium had dissolved and was then cooled to room temperature. About 250 cc. of water was added to decompose the sodium ethylate and the alcohol was removed by distillation under reduced pressure. When the solution became quite concentrated another 50 cc. of water was added and distillation continued until all of the alcohol was removed. The strong sodium hydroxide solution containing the β-piperidyl carbinol was extracted with five 500-cc. portions of ether. The ether was distilled off and the residual amino alcohol was distilled under reduced pressure. The yield was 14–15 g. (4043% of the theoretical amount) of a product which is a thick, viscous oil; b. p. 106–107° (3.5 mm.); d_4^{20} = 1.0263; n_D^{20} = 1.4964; M_D, calcd., 32.74; observed, 32.69.

Anal. Subs., 0.1853: H_2O, 0.1908; CO_2, 0.4254. Calcd. for $C_7H_{18}ON$: H, 11.45; C, 62.61. Found: H, 11.52; C, 62.61.

In a similar way 47.1 g. of ethyl nipecotate in 450 cc. of absolute ethyl alcohol was reduced with 46 g. of sodium to give 17–19 g. (49–55% of the theoretical amount) of β-piperidyl carbinol.

General Procedure for the Preparation of **N-Alkyl-β-piperidyl Carbinols.**—In a 500-cc. three-necked, round-bottomed flask, fitted with a reflux condenser, a mechanical stirrer and a separatory funnel, was placed 23 g. (0.2 mole) of β-piperidyl carbinol dissolved in 100 cc. of benzene, and 0.1 mole of alkyl bromide or iodide dissolved in about 75 cc. of benzene was added through the separatory funnel. With methyl iodide, ethyl iodide and allyl bromide the reaction went rapidly and heat was liberated. The reaction mixture was then stirred at room temperature for about eight hours to complete the reaction. When isopropyl bromide or *n*-butyl bromide was used the reaction was much less vigorous and the reaction mixture was stirred and heated on the steam cone for about five hours. During the mixing of the halide and the amine, a gummy material consisting of a mixture of the hydrochlorides of β-piperidyl carbinol and the N-alkyl-β-piperidyl carbinol separated from the solution.

When the reaction was complete, the mixture was made strongly alkaline by the addition of 30% sodium hydroxide solution. The benzene layer was separated and the aqueous layer was extracted with two 100-cc. portions of benzene. The benzene was distilled and the residue distilled under reduced pressure. A sample of the distillate was titrated with standard acid to determine the mean molecular weight of the mixture of alkylated and unalkylated carbinol. Then sufficient benzoyl chloride was added to the benzene solution of this mixture to react with the unalkylated material to form an amide. After standing for a few hours to allow complete reaction to occur, the N-alkyl-β-piperidyl carbinol was extracted from the benzene with dilute hydrochloric acid solution. The N-alkyl carbinol was then liberated as the free base by the addition of sodium hydroxide solution and was extracted with two 100-cc. portions of benzene. The benzene was distilled off and the residue then distilled under reduced pressure. The average yield of the alkylated carbinol was about 60% of the theoretical amount. The physical properties and analyses of the N-alkyl-β-piperidyl carbinols are given in Table II.

TABLE II

PROPERTIES AND ANALYSES OF N-ALKYL-β-PIPERIDYL CARBINOLS

Alkyl group	B. p., °C.	d_4^{20}	n_D^{20}	M_D, calcd.	M_D, obs.	Subs. g.	Cc. of 0.1116 N HCl	% N, calcd.	Found
Methyl	110–112 (7 mm.)	1.0125	1.4988	37.8	37.39	0.1743	12.1	10.85	10.84
Ethyl	110–111 (6.5 mm.)	09904	1.4911	42.42	41.86	.2929	18.55	9.79	10.05
Isopropyl	93–94 (3.5 mm.)	.9881	1.4916	47.04	46.03	.2198	12.23	8.91	8.97
n-Butyl	100–102 (4 mm.)	.9484	1.4838	51.66	51.42	.1039	5.4	8.18	8.14
Allyl	110–111 (7 mm.)	.9873	1.4982	46.57	46.00	.1990	11.6	9.04	9.11

Preparation of the **N-Alkyl-β-piperidyl *p*-Nitrobenzoate** Hydrochlorides.—To 0.1 mole of N-alkyl-β-piperidyl carbinol dissolved in 100 cc. of benzene in a 500-cc. two-necked flask, fitted with a reflux condenser and a mechanical stirrer, was added 0.15 mole of *p*-nitrobenzoyl chloride. The mixture was heated on the steam cone and stirred for three hours, during which time a gummy mass separated. About 200 cc. of water containing a little hydrochloric acid was added and the benzene layer was separated. The water layer was extracted with two 100-cc. portions of ether and then made alkaline by the addition of cold sodium hydroxide solution. The oily *p*-nitrobenzoic acid ester which separated was collected in ether and the ether solution acidified with alcoholic hydrogen chloride. The nitro ester hydrochlorides usually separated as gummy solids and were purified by crystallization from absolute alcohol. The yields were about 50% of the theoretical amount. The properties of the compounds are indicated in Table III.

TABLE III

PROPERTIES AND ANALYSES OF THE N-ALKYL-β-PIPERIDYL CARBINOL *p*-NITROBENZOATE HYDROCHLORIDES

Alkyl group	M. p., °C. (corr.)	Subs., g.	Cc. of 0.09744 *N* $AgNO_3$	Empirical formula	Cl, calcd.	Cl, found
Methyl	187–190	0.1598	5.13	$C_{14}H_{19}N_2O_4Cl$	11.27	11.09
Ethyl	194–195	.1537	4.83	$C_{15}H_{21}N_2O_4Cl$	10.79	10.86
Isopropyl	196–200	.1566	4.62	$C_{16}H_{23}N_2O_4Cl$	10.34	10.19
n-Butyl	197–198	.1537	4.36	$C_{17}H_{25}N_2O_4Cl$	9.94	9.80
Allyl	186–187.5	.1491	4.5	$C_{16}H_{21}N_2O_4Cl$	10.41	10.43

Preparation of the N-Alkyl-p-piperidyl Carbinol *p*-Aminobenzoate Hydrochlorides.—To a solution of 0.05 moles of the nitro ester hydrochloride in 200 cc. of absolute alcohol was added 0.25 g. of platinum oxide catalyst[3] and then this mixture was treated with hydrogen at about two atmospheres' pressure. The pressure gage indicated that the theoretical amount of hydrogen was absorbed in ten minutes but the reducing conditions were maintained for about forty-five minutes. The mixture was filtered to remove the catalyst and the alcoholic solution was concentrated under reduced pressure to about 75 cc. About 300 cc. of dry ether was added and the solution was cooled in an ice-salt bath. A gummy solid separated which was obtained crystalline by recrystallization from alcohol-ether mixtures. These crystals were usually slightly yellow. The color could not be removed by treating the alcoholic solution with decolorizing carbon (Norit) but by treating a second time with hydrogen in the presence of the platinum catalyst, white or only slightly yellowish products were obtained. In every case a considerable amount of gummy material which could not be crystallized was obtained. The average yield of crystalline material was about 45% of the theoretical amount. The physical properties and analyses of the products are listed in Table IV.

TABLE IV

PROPERTIES AND ANALYSES OF THE N-ALKYL-β-PIPERIDYL CARBINOL *p*-AMINOBENZOATE HYDROCHLORIDES

Alkyl group	M. p., °C. (corr.)	Subs., g.	Cc. of 0.0999 *N* $AgNO_3$	Empirical formula	Cl, calcd.	Cl, found
Methyl	174–177	0.1807	6.31	$C_{14}H_{21}O_2N_2Cl$	12.46	12.38
Ethyl	188–190	.1804	6.07	$C_{15}H_{23}O_2N_2Cl$	11.87	11.93
Isopropyl	235.5–237.5	.1890	6.00	$C_{16}H_{25}O_2N_2Cl$	11.33	11.24
n-Butyl	205–207	.1911	5.83	$C_{17}H_{27}O_2N_2Cl$	10.85	10.82

Summary

1. Methods for the preparation of β-piperidyl carbinol and its N-alkyl derivatives have been devised.
2. The *p*-aminobenzoate hydrochlorides of these alkyl carbinols have been prepared.
3. Pharmacological tests show that these aminobenzoyl ester hydrochlorides have relatively low toxicity and strong local anesthetic action.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

STUDIES IN AUTO-OXIDATION. I. CYCLOHEXENE PEROXIDE. (PRELIMINARY COMMUNICATION)[1]

BY H. N. STEPHENS

RECEIVED NOVEMBER 18, 1927 PUBLISHED FEBRUARY 4, 1928

'She formation of peroxides, or moloxides, as intermediate products in auto-oxidation processes was suggested almost simultaneously, in 1897, by the theory of Bach[2] and that of Engler and Wild.[3] Although in some cases experimental confirmation of their views has not been as specific as might be desired, their fundamental ideas have grown in favor up to the present time. In numerous cases of substances undergoing auto-oxidation, tests characteristic of peroxides have been obtained, but in nearly all cases the isolation of the particular substances responsible for these tests has not been realized. One notable exception is offered by the intermediate product in the oxidation of benzaldehyde, which was recently isolated by Jorissen and Van der Beek.[4] Although this substance, benzoyl hydroperoxide, had been known for some years,[5] previous attempts to isolate it in the auto-oxidation of benzaldehyde had resulted in failure.

In the case of substances containing the ethenoid linkage, the isolation of intermediate peroxides has presented still more difficulty, and repeated failures by various investigators to isolate these products have gradually strengthened the view that the primary auto-oxidation products are unisolable. Substances which corresponded in empirical composition to peroxides have been isolated by Engler and Frankenstein[6] and Staudinger[7] but in neither case were the characteristic reactions of peroxides shown. According to Staudinger, his product was formed from the monomolecular peroxide by polymerization, through oxygen-to-oxygenlinkages, to a product of indefinitely large molecular weight.

For complete confirmation of the theory of peroxide formation, it is, of course, necessary to isolate the primary intermediate products, and with this end in view the present research was started about four years ago. In choosing an unsaturated hydrocarbon for use as a starting material the main requisites were simplicity of structure and reasonable activity toward gaseous oxygen and it was found that cyclohexene fulfilled the

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[1] This paper describes the first of a series of investigations on the auto-oxidation of substances containing the ethenoid linkage, the primary purpose being a study of the mechanism of these reactions.

[2] Bach, *Compt. rend.*, 124, 951 (1897).

[3] Engler and Wild, *Ber.*, 30, 1669 (1897).

[4] Jorissen and Van der Beek, Kec. *trav. chim.*, 45, 245 (1926).

[5] Baeyer and Villiger, *Ber.*, 33, 858, 1569 (1900).

[6] Engler and Frankenstein, *Ber.*, 34, 2933 (1901).

[7] Staudinger, *Ber.*, 58, 1075 (1925).

latter requirement to a greater extent than the simple, open chain hydrocarbons.

Continuous bubbling of oxygen through this hydrocarbon was obtained by means of a circulator previously described by the writer.[8] By this means exposure of a fresh surface of liquid was assured at all times. Oxidation was carried out at room temperature under an average pressure of about 1 atmosphere of oxygen and the duration of experiments varied between one and four months.

The crude product of oxidation in each case showed only a faint yellow coloration and its viscosity varied with the time of oxidation. It was at once noted that the liquid gave a pronounced peroxide reaction but it was evidently a mixture containing a considerable amount of unchanged cyclohexene. After distilling the latter off under reduced pressure, a sirupy residue was obtained from which it was attempted to separate the peroxide. After several unsuccessful attempts it was found that the liquid showed very little tendency to decompose on moderate heating, so distillation under very low pressures was attempted. By using a pressure of about 0.5 mm., it was found that even early in the distillation a peroxide test was given by the distillate. By following the intensity of the color produced by one drop of the distillate with 2 cc. of titanic sulfate solution, the fraction richest in peroxide was secured and this submitted to further fractional distillation. Finally a liquid was obtained which boiled, under 0.5 mm. pressure, at 54–56°. The quantities of this liquid, obtained from various experiments, were always very small, the largest amount being approximately 6 g. This latter amount was the product from 800 g. of cyclohexene which had been oxidized over a period of four months.

Cyclohexene peroxide is a colorless, mobile liquid with a pungent odor strongly reminiscent of oxidizing substances such as ozone, nitrogen pentoxide, hypochlorous acid, etc. It has a corrosive action on the skin, which manifests itself after contact for only a few seconds. If allowed to remain on the skin for some time, it produces burns which take several days to heal. The peroxide colors titanic sulfate solution instantly, liberates iodine from acidified potassium iodide and decolorizes indigo solution; in brief, it behaves as a typical organic peroxide. Analysis of the peroxide gave values as follows.

Anal. Calcd. for $C_6H_{10}O_2$: C, **63.16;** H, 8.77. Found: C, **63.26, 63.22; H.** 8.88, **8.86.**

A molecular weight determination in benzene, by the Maass modification of the Beckmann cryoscopic method,[9] gave a value of 119, while the theoretical value is 114. Determination of active oxygen iodimetrically was unsatisfactory, as the liberated iodine apparently reacted with the reduc-

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[8] Stephens, *Ind.* Eng. Chem., **19,426** (1927).

[9] Maass, *Trans. Roy. Soc. (Canada) 13,* Sec. iii, 97 (1919).

tion product. Reduction with stannous chloride also failed to give the expected results but the values obtained by the latter method were concordant. Analysis of three different samples of peroxide gave values corresponding to 78.7 – 79.8% of the theoretical amount of active oxygen. The agreement between these different analyses must indicate either a constant amount of impurity or a constant amount of side reactions during reduction. The latter does not seem very plausible, as one would expect slight variations in technique to cause variations in the extent of side reactions.

The analytical values for carbon and hydrogen require that any impurity present have the same composition as the peroxide and there are two possible ways of accounting for the existence of such an impurity. First, polymerization or some similar reaction may take place in the vapor phase and the impurity may thus be carried over into the distillate. Second, if we accept the existence of two modifications of the peroxide,[10] one labile and one stable, we might assume that their boiling points were so close together as to render them inseparable by distillation. The possibility of the existence of two forms of cyclohexene peroxide is one which will be studied in this Laboratory in the near future.

The other possibility, that of polymerization, is one which has already been investigated in a preliminary way. After each fractionation of cyclohexene peroxide, it was noticed that a considerable residue of sirupy liquid remained which could not be distilled. An examination of the empirical composition of this liquid showed it to be practically identical with the peroxide.

Anal. **Calcd. for** $C_6H_{10}O_2$: C, 63.16; H, 8.77. **Found:** C, 63.17, 62.58; H, 8.46, 8.53.

Determination of the molecular weight in benzene as above, gave a value of 215, whereas $(C_6H_{10}O_2)_2$ requires 228. It seems probable, then, that at the temperature of distillation, two molecules of peroxide may combine, by polymerization or condensation, to form a product or products of the same empirical composition. It is rather interesting to note, in passing, that Harries[11] obtained two ozonides of cyclohexene, only one of which was distillable.

In examining further the sirupy liquid obtained from the peroxide, it was found that, although it produced no coloration of titanic sulfate at room temperature, except after long contact, a strong color developed on heating the mixture. As the substance is very slightly soluble in water, the function of the heat may be to increase the solubility or to cause the dissociation of an unstable polymer. If this product were a single substance, formed from two molecules of peroxide, it would be expected that one peroxide group would be left as such and therefore one would ex-

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[10] Staudinger, *J. prakt. Chem.*, 85, 330 (1912).

[11] Harries, *Ann.*, 410, 25–26 (1915).

pect to find $^1/_2$ the amount of active oxygen required by the monomolecular form. The actual value obtained was 34% instead of 50% but, as will be brought out in detail in later papers, there are possible reactions which would use up active oxygen without changing the empirical composition and there is no reason for believing the sirupy liquid to be the product of a single reaction. However, the existence in the product of a considerable proportion of a substance having peroxide properties seems to point to the possibility of a condensation of two molecules of the simple peroxide, in which one peroxide group is left as such. This would involve an entirely different type of reaction from that postulated by Staudinger to account for his polymeric peroxide.

Investigations in this field are being extended along a number of different lines and further communications will be published in the near future.

Summary

1. For the first time, a true peroxide has been isolated as a product of auto-oxidation of an unsaturated hydrocarbon. Thus, specific confirmation has been obtained for the Bach-Engler interpretation of the action of oxygen on the ethenoid linkage.

2. Evidence has been obtained which shows that there is a tendency for two molecules of peroxide to combine, forming a new substance with peroxide properties.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A PREPARATION METHOD FOR BENZOPHENONE

BY GREGG DOUGHERTY

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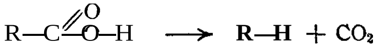
Introduction and Discussion

It is well known that simple carboxylic acids yield hydrocarbons to a greater or less extent when they are heated with finely divided metals, particularly copper and nickel.



$$R{-}\overset{\overset{O}{/\!/}}{C}{-}O{-}H \longrightarrow R{-}H + CO_2$$

In the case of aliphatic acids the reaction is usually difficult to effect. Acetic acid, for example, when heated with copper at 390–411°, gives mainly acetone and when nickel is used as the catalyst a considerable portion of the acid is decomposed into complex carbonaceous substances.[1] With aromatic acids the decomposition is usually easier but frequently, as with benzoic acid and nickel,[2] the reaction temperature is so high that the resulting hydrocarbons are largely transformed into other substances.

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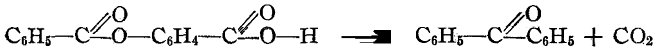
[1] Sabatier and Senderens, *Ann. chim. phys.*, [8] 4, 467 (1905).

[2] Sabatier and Mailhe, *Compt.* rend., 159, 217 (1914).

It has been found that this process of eliminating carbon dioxide from an acid can be used to advantage in the preparation of benzophenone from o-benzoylbenzoic acid.



$$C_6H_5—C(=O)—O—C_6H_4—C(=O)—O—H \longrightarrow C_6H_5—C(=O)—C_6H_5 + CO_2$$

The yields, 80–90% of the theoretical, exceed the average of those obtained by the Friedel and Crafts synthesis, in which benzene and benzoyl chloride react in the presence of aluminum chloride, by about 10%. Furthermore o-benzoylbenzoic acid, which is the intermediate in the synthetic anthraquinone process, is manufactured on a large scale and should be obtained without difficulty. It can also be prepared easily and inexpensively from phthalic anhydride, benzene and aluminum chloride.[3] This reaction goes nearly to completion, 95–97%, so that the yield of benzophenone based on the phthalic anhydride is still somewhat better than that obtained when benzoyl chloride and benzene are used, and the cost of the materials is much less.

When o-benzoylbenzoic acid is heated alone to about 300° some carbon dioxide is eliminated and benzophenone can be detected among the products. The yield, however, is negligible. The catalysts which accelerate the reaction most efficiently are metals such as copper, nickel, iron and the o-benzoylbenzoic acid salts of these metals. It is not necessary that the metals be particularly finely divided as they go into solution in the acid, and the only apparent advantage in having a fine state of subdivision is to increase the rate of solution. The preferred catalysts are finely divided copper and the copper salt of o-benzoylbenzoic acid. The latter is easily made by adding a copper sulfate solution to a solution of the sodium salt of the acid, washing, filtering and drying the precipitate at 110°. The velocity of the reaction increases with the amount of catalyst used, but too large a quantity causes inconvenience in getting out the product. It has been found that a satisfactory ratio is **1-3** g. of copper, or an amount of the copper salt of o-benzoylbenzoic acid containing an equivalent weight of copper, to 100 g. of the acid. In the presence of these catalysts carbon dioxide elimination begins at about 150° and increases as the temperature rises until 306° is reached, when the reaction mixture begins to boil. The speed of the reaction below 200° is too slow for practical purposes and above 280° there is decomposition, the formation of anthraquinone and unidentified tarry substances. The optimum temperature range is about 250–270°.

Preparation Procedure

Three hundred grams of pure o-benzoylbenzoic acid was placed in a distilling flask with a low side tube. To this was added 20 g. of the copper salt of the acid. The flask was fitted with a mechanical stirrer

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[3] Cain, "The Manufacture of Intermediate Products for Dyes," Macmillan and Co., London, 1918, p. 240.

arranged through a mercury seal, and a thermometer the bulb of which was immersed in the liquid when the material melted. The mixture was heated with stirring; carbon dioxide evolution was appreciable at 200°, and it was allowed to escape through the side tube of the flask and to bubble through water, which gave an indication of the progress of the reaction. The temperature was allowed to rise and was maintained at 260° until carbon dioxide evolution ceased (about four hours). It is necessary to continue until the carbon dioxide evolution has completely stopped. If a distillation is attempted before this point, a considerable quantity of anthraquinone is formed, which contaminates the product. The stirrer was taken from the flask, a short air condenser attached to the side tube and the thermometer raised out of the liquid as for distillation. The crude benzophenone was distilled over until the drops of distillate became dark in color; the weight of this crude product was 209 g., 86.6% of the theoretical. One crystallization from 95% alcohol gave pure benzophenone, m. p. 47-48', in an amount corresponding to 82-84% of the theoretical based on the o-benzoylbenzoic acid. The crystallization may be replaced by distillation in a vacuum.

Summary

A method for the preparation of benzophenone has been described.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND CO.]

THE ACTIVE PRINCIPLES OF THE POSTERIOR LOBE OF THE PITUITARY GLAND.[1] I. THE DEMONSTRATION OF THE PRESENCE OF TWO ACTIVE PRINCIPLES. II. THE SEPARATION OF THE TWO PRINCIPLES AND THEIR CONCENTRATION IN THE FORM OF POTENT SOLID PREPARATIONS

BY OLIVER KAMM, T. B. ALDRICH, I. W. GROTE, L. W. ROWE AND E. P. BUGBEE

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Introduction

The manifold physiological activities of extracts of the posterior lobe of the pituitary gland are now well known; namely, their effect in stimulating uterine contractions (oxytocic activity), their ability to raise the blood pressure (pressor activity), and their diuretic-antidiuretic effects (renal activity). These three types of activity have led the way to three definite and important medical applications; these are illustrated respectively by the use of pituitary solutions in obstetrics, in the treatment of surgical shock, and in the control of diabetes insipidus.

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[1] Presented before the Detroit meeting of the American Chemical Society, September, 1927.

On the other hand, chemical information concerning the physiologically active constituents of pituitary extracts is rather meager; in fact it has not been shown definitely whether the above enumerated pharmacological activities are due to a single chemical substance (hormone) or to the presence of several different compounds. The American investigators, and this is true especially of the Johns Hopkins and the U. S. Hygienic Laboratory groups, have defended the evidence favoring a single active principle, whereas the English workers have argued for two or three principles, while the Germans at one time claimed the separation of even a larger number.

Our own work has been directed towards the isolation of the active principle (or principles) in pure form in the hope that something might be learned concerning its chemical nature. Assuming the presence of a single hormone, it is obvious that the same result will be attained irrespective of the particular method chosen for analysis. In our own experience the pressor assay method is capable of an accuracy of 10%, the oxytocic assay method of 10 to 20%, while the diuretic method is scarcely adapted to quantitative work. Because of its greater accuracy we adopted the pressor assay method and proceeded with the concentration of the active principle.

As a result of a new method of manipulation to be described presently, we succeeded in preparing a very potent product—in fact when this fraction was tested by the pressor assay method it appeared to be many times as potent as the very active product reported by Abel, Rouiller and Geiling,[2] although an accurate comparison could not be made. However, when this potent product was subjected to an accurate assay by the oxytocic method it was found that most of the smooth-muscle-stimulating principle had disappeared—either it had been eliminated in the fractionation process or it had been destroyed. Accordingly the work was repeated and all fractions, residues and solutions normally discarded were carefully reexamined. As a result an efficient method was developed for the separation of the pressor from the oxytocic activity.

This illustrates the necessity of applying more than one quantitative assay method in any attempt at fractionation and concentration of extracts of the posterior lobe—a requirement that has been disregarded by most workers in this field. However, in demonstrating the presence of more than one active principle it is necessary not merely to obtain fractions that differ from each other when subjected to two or more methods of assay (since this result might be due to the partial injury of a single active principle), but it is necessary to obtain complete quantitative evidence to demonstrate that a separation can be effected, and by recombining the fractions in the original proportions it should be possible to obtain again a pituitary solution indistinguishable from the original, thus proving that

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[2] Abel, Rouiller and Geiling, *J. Pharmacol.*, 22, 289 (1923).

no injury of any active principle has taken place. This is exactly what we have done and, in addition, by continuing our fractionation process, we have effected the first substantially complete separation of two principles. Our diuresis experiments on rabbits seem to indicate that the diuretic principle is the same as the pressor principle, thus eliminating one of the complicating possibilities. In addition, we have obtained both principles (oxytocic and pressor) in highly potent form as solid preparations although not yet in crystalline condition. No definite chemical information is available at the present time concerning the chemical nature of these principles but they appear to be basic in character. For this reason we have designated them as alpha- and beta-hypopharnines[3] (amines derived from the hypophysis).

Historical Part

The pressor action of extracts of the pituitary gland was discovered by Oliver and Schafer[4]; and later Howell" and Schafer and Vincent%-ere able to demonstrate that the pressor action is confined to the posterior lobe.

The Epinephrine Theory.—Since epinephrine (adrenaline) was the most active pressor compound known to occur in the animal organism, it was logical to suspect that pituitary extracts owe their blood-pressure-raising effect to an action on the suprarenal glands, whereby an increased amount of epinephrine is discharged into the circulation, or that a compound similar to epinephrine or that epinephrine itself occurs in the pituitary gland. In spite of the fact that Dale[7] had concluded in 1909 that epinephrine and the active principle of the posterior lobe are two different substances, the epinephrine theory was not readily abandoned; in fact, as recently as 1916 Watanabe and Crawford[S] concluded that "pituitary extracts when prepared by certain methods, yield color reactions which would suggest the presence of epinephrine or an epinephrine-like compound."

The Histamine Theory.—In 1919 Abel and Kubota[g] isolated histamine from a quantity of whole pituitary gland and on the basis of their chemical and pharmacological studies concluded that "histamine is the plain-muscle-stimulating and depressor constituent of the posterior lobe of the pituitary gland. The physiological and chemical evidence in favor of identity of

[3] These products are already being manufactured for experimental clinical use a-Hypophamine is being supplied under the trade name of Oxytocin (designating quick birth) and β-Hypophamine under the trade name Vasopressin (designating elevation of blood pressure). They were first supplied for clinical use in August, 1927.

[4] Oliver and Schafer, J. *Physiol.,* 18, 277 (1895).

[5] Howell, J. *Exp. Med.,* 3, 246 (1898).

[6] Schafer and Vincent, J. *Physiol.,* 25, 87 (1899).

[7] Dale, *Biochem.* J.,4, 427 (1909).

[8] Watanabe and Crawford, J. *Pharmacol.,* 8, 75 (1916).

[9] Abel and Kubota, *ibid.,* 13,243–298 (1919).

the two principles coincide at every point." A separate pressor principle of minor importance was also recognized.

The claims of Abel and Kubota were promptly and effectively disproved by Dudley[10] in a masterly piece of experimental work. Histamine is stable towards alkali; it is unacted upon by trypsin; it is soluble in boiling chloroform but not readily extracted from acid solutions by butyl alcohol. The pituitary uterine stimulant exhibited exactly the opposite behavior in each one of these tests. In a subsequent paper by Abel and Nagayama[11] the Histamine Theory was withdrawn.

The Single versus the Multiple Hormone Theories.—In addition to the three primary physiological responses that have been obtained by the administration of pituitary extracts (oxytocic, pressor and renal activities) a number of additional effects have been reported, as for example the melanophore action, the galactagog action, the effect on coagulability of the blood, the effect on intestinal peristalsis, inhibition of gastric secretion, mydriasis, etc. It was natural therefore to consider the possibility of the presence of a variety of active principles and such a possibility has not been overlooked by the earlier workers.

Schafer and Vincent[12] showed that pituitary extracts contain a depressor as well as a pressor substance, and as early as **1900** Osborne and Vincent[13] called attention to the fact that the central portion of the posterior lobe appeared to contain more activity than the periphery. Herring[14] and more recently, Hogben and De Beer,[15] have sought to trace the active principles to physiologically distinct parts of the posterior lobe.

Führer[16] in **1913** claimed to have isolated four crystalline principles from the posterior lobe but this work has never been verified by others.[17] It is likely that these crystalline fractions consisted of inorganic salts containing in admixture appreciable and variable amounts of physiologically active material.

Not only did Dudley[10,18] overthrow the "histamine theory," but he went farther and offered evidence suggesting the presence of more than one active principle. By means of butyl alcohol extraction of dilute aqueous pituitary solutions, Dudley was able to secure what appeared to be a partial separation of the oxytocic and pressor activities, although considerable decomposition took place.

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[10] **Dudley, J.** *Pharmacol.*, **14,** 295–312 (1919).

[11] **Abel and Nagayama,** *ibid.*, 15, 347–399 (1920).

[12] **Schafer and Vincent, J.** *Physiol.*, **25,** 87 (1899).

[13] **Osborne and Vincent,** *Brit. Med.* **J.,** 1, 502 *(1900).*

[14] **Herring,** *Quart. J. Exp. Physiol.*, 1, 149 (1908); 6, 107 (1913).

[15] **Hogben and De Beer,** *ibid.*, 15, 163 (1925).

[16] **Führer,** *Z. ges. exp. Med.*, 1, 397 (1913).

[17] **Abel and Pincoffs,** *Proc. Nat. Acad. Sci.*, **3,** 507 (1917).

[18] **Dudley, J.** *Pharmacol.*, **21,** 103 (1923).

In contrast to the claims of Fühner, Guggenheim[19] offered evidence in favor of the unitarian theory. He found that the various physiological activities of pituitary extracts (the vasomotor, respiratory and oxytocic) are all destroyed equally readily upon exposure to alkali.

Since 1920 Abel and his co-workers have been the enthusiastic advocates of the unitarian theory. Although they refer to three products, A, B and C derivable from the posterior lobe, the latter two, a histamine-like substance and histamine itself, appear in animal extracts of all kinds. However, in respect to Compound A they concluded[20] that "the infundibulum contains but one active specific substance, or hormone, and that this in its uninjured state is not only a blood-pressure-raising but also a plain-muscle-stimulating substance." Their most recent publication[2] states that "we therefore conclude that all the evidence at hand is greatly in favor of our belief that the oxytocic?, pressor, diuretic and respiratory activities referred to above are properties of one and the same substance."

The wealth of evidence presented in favor of the unitarian nature of Compound A is almost incontrovertible. Subjected to four different agencies, namely, heat, tryptic digestion, hydrochloric acid decomposition and alkaline hydrolysis, both the pressor and oxytocic activities disappeared as in the decomposition of a single compound. Finally, even more convincing evidence is claimed in the statement that in their highly purified products the pressor, oxytocic and diuretic activities stand in the same relationship as in an ordinary pituitary extract.

Recently Smith and McClosky[21] demonstrated the parallel destruction of the oxytocic and pressor activities by heat and thus claimed to have affirmed the evidence advanced by Abel in favor of chemical unity. Finally, in a study "On the Dialysis of the Physiologically Active Constituents of the Infundibulum" the same workers[22] summarized the situation thus: "The identical diffusion rate of the oxytocic, pressor and renal activities present in infundibular extracts argues in favor of their chemical identity, and confirms the view held by Abel and his collaborators on this matter."

The controversy between Dudley and Abel has been submitted to analysis by Hogben, Schlapp and MacDonald,[23] and although these investigators were not disposed to regard Abel's preparation as a pure homogenous substance, they likewise stated that "we cannot regard Dudley's conclusions as fully established until his fractions have been standardized by a method of comparison such as we here propose."

[19] Guggenheim, *Biochem. Z.*, 65,189 (1914); 81,277 (1917).

[20] Abel and Rouiller, J. *Pharmacol.*, 20, 65–84 (1922).

[21] Smith and McClosky, *Hyg. Lab. Bull.*, No. 138, April, 1924.

[22] Smith and McClosky. J. *Pharmacol.*, 24,391 (1924).

[23] Hogben, Schlapp and MacDonald, *Quart. J. Exp. Physiol.*, 14,315 (1924).

In subsequent publications by Schlapp[24] and more recently by Draper[25] an account is given of a successful repetition of Dudley's experiment and an additional new method is presented by Schlapp in support of the multiple hormone theory. "By producing precipitates of lead sulfide in extracts by the passage of sulphuretted hydrogen gas through suitable concentrations of lead acetate all the active principles are to some extent absorbed. But the quantity of pressor and melanophore substance absorbed exceeds that of oxytocic absorbed by a significant amount."

Dreyer and Clark[26] as well as Fenn[27] have considered the melanophore stimulant as a separate principle but according to Schlapp[24] there is insufficient quantitative evidence that the pressor and melanophore responses are due to distinct substances.

It has been suggested that several pressor principles are present in posterior lobe pituitary extracts. Crawford[28] was primarily interested in the concentration of this type of activity but even in 1916 when he was still investigating the possibility of the presence of epinephrine he suggested that "in pituitary extracts there must be one or two depressor compounds, and one or more pressor compounds." Dudley[LY] has also presented evidence suggesting the presence of a second pressor principle.

The present status of the work on the isolation of the active principles of the posterior lobe is thus expressed by Dudley:[29] "I am driven, therefore, to the conclusion that Abel and Rouiller's preparation, like my own, contained at least three, and possibly more, active substances mixed with an unknown quantity of inert material."

"My conclusion, I am aware, shows the prospect of isolating the pituitary active principles in a far less encouraging light than theirs; but the experience of the past few years has given me so strong an impression of the difficulties entailed in the search for this group of extremely active, unstable substances, present in relatively minute proportions in the scarce and costly material of the posterior lobe of the pituitary gland, that I feel it a duty to make clear, for the benefit of other workers on the subject, my own reading of the facts at present available."

General Discussion

In reading over the extensive experimental work that has been reported in connection with the search for the active principle (or principles) of the posterior lobe of the pituitary gland one is impressed by the great number of uncorrelated experiments. For this reason we shall attempt to present

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[24] Jchlapp, *Quart. J. Exp. Physiol.*, 15, 327 (1925).

[25] Draper, *Am. J. Physiol.*, **80, YO** (1927).

[26] Dreyer and Clark, **J.** *Physiol.*, **58,** xviii (1024)

[27] Fenn, *ibid.*, ***59*****,** xxxv (1924).

[28] Crawford, **J.** *Pharmacol* **, 15,** 81 (1920); 8, 75 (1916)

[29] Ref. 18, p. 121.

only the essential parts of our work but we shall endeavor to describe our experiments in sufficient detail so that the results can readily be duplicated.

Obviously it will be impossible to present here the hundreds of kymograph charts upon which our work is based even if it were desirable to do so. We can assure the reader, however, that none of our assays are based upon one or two contractions of a muscle in comparison with a standard solution or upon one or two blood-pressure readings. Samples submitted for assay were treated as unknowns and often checks were required from two workers. A brief account of the assay methods is given below.

Fortunately there is now available from the U. S. Bureau of Chemistry a Standard Powdered Pituitary Product and all oxytocic results can be expressed in terms of this standard. The official Solution of Pituitary of the Pharmacopeia of the United States represents in each cc. the activity derived from **3** mg. of this standard powder. The potency of this solution may be expressed in terms of International Units,[30] each cc. being equivalent to 10 International Oxytocic Units. It follows, therefore, that one milligram of the U.S.P. Standard Powdered Pituitary is equal to 2 International Units of oxytocic activity.

In all of our work we refer to the U.S.P. Standard Powdered Pituitary as possessing a potency of 100%. A product, therefore, that is reported as 1000% is 10 times as potent as the U.S.P. standard and contains 20 Units per milligram.

A Pressor Standard

The Pharmacopeia fixes only an oxytocic standard and obviously this would be sufficient if all of the activity of pituitary extracts were due to a single principle, as has been supposed by several of the leading investigators. In view of the fact that we have definitely separated two principles, the need of a Pressor Standard becomes apparent.

In working with fairly fresh pituitary glands we find that there is a surprising constancy in the relative amounts of pressor and oxytocic activities present in the gland, and indeed it is this constancy that has aided in promulgating the ideas of a single principle.

For the present we propose that the pressor standard be expressed also in terms of the U.S.P. Standard Powdered Pituitary Product, one milligram of this powder being considered as containing 2 Pressor Units. The official solution of pituitary would therefore be designated as containing 10 International Units of Oxytocic activity and also 10 Pressor Units.

In the subsequent work we shall refer to the U.S.P. Standard Powdered Pituitary as possessing a pressor potency of 100%. A fraction, therefore, that is reported by us as 5000% is fifty times as potent as the U.S.P. standard and contains 100 Pressor Units per milligram.

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[30] League of Nations, p. 14 of report by Second International Conference on the Biological Standardization of Certain Remedies, Geneva, Aug 31—Sept. **3,** 1925.

The Oxytocic Assay Method

The oxytocic method of assaying pituitary solution depends upon the measurement of the contraction caused in a strip of uterine muscle when it is immersed in Locke's solution to which has been added some of the solution to be tested. This method was first suggested by Dale and Laidlaw.[31] The apparatus consists of a water-bath in which a temperature of 37.5° is maintained by an electric heating unit controlled by a thermostatic regulator. Partly immersed in the water-bath stands a vertical tube of about 150 cc. capacity marked at the 100cc. level. Locke's solution, previously heated to 37.5°, is run into the vertical tube up to the 100cc. level through a small tube near the lower end. The Locke's solution may be drained off conveniently through a second small tube in the lower end of the vertical tube. Air is bubbled slowly through the Locke's solution from a small glass tube which enters the upper and open end of the vertical tube and extends down almost to the bottom of the solution. The extreme tip of the air tube is bent into a hook shape. This hook furnishes a convenient place for the attachment of one end of a strip of muscle. A thread is attached to the other end of the muscle and in turn is attached to a light lever which bears against the smoked paper of a kymograph. In this way the contractions and relaxations of the muscle are recorded on the smoked paper. The most satisfactory uterine muscles are taken from virgin guinea pigs weighing from 200 to 250 g. Two strips are obtained from each guinea pig.

In making an oxytocic test a measured amount of a pituitary solution is added to the 100 cc. of Locke's solution in which the uterine muscle is immersed. The muscle contracts very quickly and relaxes again in a few minutes. The Locke's solution is then drained away and fresh Locke's solution is admitted up to the 100cc. mark. After a few minutes' rest the muscle may be used for another test. Various quantities of a standard pituitary solution of known strength are tried on the muscle until the dosage has been determined which is required to cause a contraction slightly less than the maximum contraction of that muscle. Then various quantities of the unknown solution are tried until the quantity has been found which will give a sub-maximum contraction equal to that produced by the standard solution. Then tests are made alternately with quantities of the standard and unknown solutions until the relationship between their activities has been determined.

In this Laboratory so many oxytocic tests have to be made that the original one- or two-tube apparatus proved inadequate. The apparatus has been increased in capacity by making the water-bath large enough to hold twelve vertical tubes so that twelve muscles can be used at the same time. Accurate assays are secured by testing a single extract on from three to six muscles.

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[31] Dale and Laidlaw, *J. Pharmacol.*, **4**, 75 (1912).

The Pressor Assay Method

The pressor method of assay for posterior pituitary extracts depends upon the fact that consecutive injections of the same quantity of an active extract when given intravenously to a dog—a very definite technique being followed—cause the same amount of increase in blood pressure. Some of the details of the technique are similar to those necessary for the proper standardization of adrenaline.

The procedure is briefly as follows.

A medium-sized, healthy, normal dog is deeply anesthetized with chloretone[32] by intraperitoneal administration of a dose of a 40% solution of chloretone in 40% alcohol, amounting to 0.4 g. per kg. body weight of the dog (1 cc. of the 40% solution per kg.). Cannulas are inserted into one femoral vein and one carotid artery, the former for receiving the intravenous doses of diluted extract and the latter for connection to a mercury manometer for recording arterial blood pressure. Under this deep anesthesia–all reflexes destroyed except a slight conjunctival reflex—0.04 cc. (1 cc. of a **1–25** dilution) of a standard U.S.P. Pituitary Extract is injected. Every 15 minutes, not oftener, alternately there are injected intravenously the small doses of sample and standard until comparable doses of the two are found which will produce the same rise in blood pressure on the same dog in at least two series. The result should be checked on another dog if there is any doubt about the first test.

Pituitary extracts of the posterior lobe cause a rise in arterial pressure due to constriction of peripheral blood vessels. If the above technique is rigidly followed, there will be no preliminary fall in blood pressure or development of tolerance such as occurs if larger doses are given too frequently. Special emphasis is placed upon the requirement of using only 0.4 unit for the intravenous dose.

Experimental Part

The activity (both pressor and oxytocic) of the posterior lobe of the pituitary gland may be removed almost quantitatively by extracting the gland with water containing a small amount (0.1 to 1%) of acetic acid.[33] This method, originally proposed by one of the present writers (Aldrich),[34] is now a part of the official method in the Pharmacopeia and is in quite general use by manufacturers. Nevertheless, some of the scientific workers in the field have employed ordinary aqueous extracts and apparently have failed to recognize the importance of using acidified water. This is

[32] Rowe, J. *Pharmacol.*, 9, *107* (1916); Hamilton, J. Am. *Pharm. Assocn.*, 1, 1119 (1912).

[33] The use of a highly ionized acid such as hydrochloric acid even in as low a concentration as 0.5% results in destruction of the active principles. Recent work on this point has been reported by Stasiak, J. *Pharmacol.*, 28, 1 (1926).

[34] Aldrich, *Am.* J. *Physiol.*, 21, Proc. XXIII (1908).

true, unfortunately, of the important work of Schlapp,[24] of Draper[25] and possibly of Dudley.[10]

The Importance of *P*H Control in Making Aqueous Extracts

Adams[35] has shown that considerable loss of oxytocic activity takes place when pituitary solutions are heated at a PH of 3. We find that the reaction of extracts prepared without the use of acetic acid is near a PH of 6, and that the loss of pressor activity is even more pronounced than the loss of oxytocic activity. Extracts prepared with the use of 0.25% acetic acid possess a PH of about 3.8 to 4.4 and are comparatively stable.

The following summary gives the results of extraction of 1-g. samples of acetone-desiccated posterior lobe both with 0.25% acetic acid and with distilled water, the extracts being heated during only one-half hour as in the method described below.

TABLE I

ASSAYS BASED ON 1-G. SAMPLES OF DESICCATED POSTERIOR LOBE

(a)	Extracted with 0.25% acetic acid	= 1000 units (Oxytocic)
(b)	Extracted with 0.25% acetic acid	= 800-1000 units (Pressor)
(c)	Extracted without acetic acid	= 800 units (Oxytocic)
(d)	Extracted without acetic acid	= 250 units (Pressor)
(e)	Reëxtraction of residue from (d) with 0.25% acetic acid	= 30 units (Pressor)

It is evident that more than one-half of the pressor activity was lost and, although the oxytocic activity is more stable, a 20% loss was detected here also. A significant point is that the loss of pressor activity is not recoverable by reëxtracting the gland residue—it has actually been destroyed.

The above experiment was duplicated in work on a manufacturing scale although unintentionally. In Table II, Experiments (a), (b), (c) and (d) illustrate the uniformity with which the activity is extracted under

TABLE II

YIELDS OF ACTIVITY ON A MANUFACTURING SCALE

	1 No. units pressor according to assay	2 No. units pressor extracted	3 No. units in salted out product
(a)	1,650,000	1,900,000[a]	1,300,000
(b)	1,650,000	1,650,000	1,630,000
(c)	1,650,000	1,460,000	1,600,000
(d)	1,650,000	1,800,000[a]	1,530,000
(e)	1,650,000	800,000	600,000
(f)		40,000	

[a] These two values indicate yields of more than 100%, due no doubt to errors in the assay. This is verified by the values recorded in Col. 3, which represent the yields in the next step in the process.

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[35] Adams, J. Biol. Chem., **30**, 235 (1917).

specified conditions. In Expt. (e) the acetic acid was accidentally omitted and, although the error was detected a half-hour later after the solution had been heated, and the acid was then promptly added, a considerable loss of pressor activity had taken place. Expt. (f) shows that reextraction of the gland residue failed to yield the activity that had been lost.

Loss of Activity Due to Acetone Desiccation

The acetone liquors recovered from the desiccation process contain a negligible amount of pressor activity but a considerably larger amount of oxytocic activity.

Fifty posterior lobes were dropped in 200 cc. of acetone, which is the volume prescribed in preparing the standard powder. Several hours later the acetone was poured off and replaced with fresh acetone, as prescribed. The acetone liquors were evaporated at a low temperature and the residue extracted with dilute acetic acid. The acid solution was then assayed by both oxytocic and pressor methods; 160 oxytocic units, but only 40 pressor units, were found. The desiccated gland material which was not completely defatted and not separated from coarse material by sifting assayed 50% of U.S.P. standard and contained a total of 2000 International Units.

In the above experiment the pituitary glands were collected during the afternoon, kept in the refrigerator overnight without freezing them, and dissected on the following morning.

Smith and McClosky[36] have not recorded a study of the acetone liquors obtained in connection with the preparation of their standard powder but we are informed in a private communication from Dr. M. I. Smith that only 0.4% of the oxytocic activity was lost

It appears, therefore, that there is very- little loss if the glands are desiccated within a few minutes after the death of the animal but a number of hours later sufficient acidity is developed to permit the acetone to extract 2% of the pressor activity and 8% of the oxytoric activity.

The Depressor Activity of Pituitary Extracts

Schafer and Vincent[12] not only demonstrated the presence of a depressor substance but showed that it is extractable from the glands by means of alcohol. Recent workers[37] have attached considerable significance to this depressor product, some referring to it as histamine.

When acetone-desiccated glands are extracted with absolute ethyl alcohol in a Soxhlet extractor, this depressor product is readily removed. We have tested it by three methods, as is shown in the following table.

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[36] Ref. 21, p. 16.

[37] For references see the excellent paper by Sharpey-Schafer and Macdonald, *Quart. J. Exp. Physiol.*, 16, 251–280 (1926).

TABLE III

ASSAYS BASED ON EXTRACT FROM 1 G. OF DESICCATED POSTERIOR LOBE

(a)	Colorimetric assay for histamine	<1 mg.
(b)	Blood pressure assay for histamine	<1 mg.
(c)	Oxytocic assay	80 Oxytocic units ≈ 100 mg. histamine

According to the oxytocic assay, approximately 100 mg. of histamine is indicated as being extractable from 1 g. of gland material. The blood pressure assay, however, indicates the presence of even less than 1% of this large quantity of histamine and the colorimetric test agrees in demonstrating that histamine is present only in small amounts. Two conclusions might be drawn: first, the depressor principle is not histamine but rather a substance much more potent than histamine in its oxytocic action; second, a small amount of histamine is present in the gland but in the process of alcohol extraction there is extracted simultaneously some of the true oxytocic principle.

We believe that the second conclusion is correct. Since the oxytocic principle is soluble in alcohol, there is no reason why it should not be extracted and our results show that in six hours' extraction approximately 10% of the oxytocic principle is removed.

Freshly collected pituitary glands contain very little histamine, but if this impurity is present it may be removed advantageously by salting-out methods. This is illustrated by the following experiment, in which a known quantity of histamine was intentionally added.

A pituitary extract was prepared so as to contain 20 mg. of pituitary proteins per cc. To this solution, which according to colorimetric assay contained material equivalent to less than 0.02 mg. of histamine per cc., there was added 0.5 mg. per cc. of histamine in the form of hydrochloride. Sufficient solid sodium chloride was then added to salt out the pituitary proteins and the precipitate was removed by centrifuging and purified merely by washing with a very small volume of saturated salt solution. The filtrate as well as the precipitate was then assayed colorimetrically for histamine with the following results:

Precipitate dissolved in water to original volume	0.02 mg. histamine per cc.
Filtrate (calcd. to original volume)	0.45–0.50 mg. histamine per cc.

It is apparent that histamine is readily removed by the salting-out method, the variation from the theory being within the limits of accuracy of the colorimetric method of assay when conducted in the presence of salts.

The Concentration of the Active Principles

In our choice of methods for the concentration of the active principles of the posterior lobe, we have been guided by the results obtained from a study of the dialysis of pituitary extracts. The active principles dialyze more slowly than does the known substance, adrenaline, and the suggestion has been advanced that the pituitary principles may possess a molecular weight in the neighborhood of 600.[38] Although this conclusion is specula-

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[38] Kamm, *Science*, Feb., 1928.

tive, it has proved a reliable guide. The active principles are relatively simple when compared with the protein-like material present in pituitary extracts. On the other hand, they are relatively complex when compared with most of the simpler glandular extractives, such as the inorganic salts, creatinine,[39] histamine, amino acids, etc.

The process may be illustrated by the separation of the active principles B from the mixture A B C, in which A represents low molecular weight substances and *C* represents the high molecular weight substances, such as proteins. In the absence of a specific precipitant for B, two methods of separation suggest themselves: first, *A* B can be separated from *C* and subsequently B can be fractionated from *A;* or, second, *A* can be separated from B *C* and subsequently B can be fractionated from *C*.

The method that we attempted to use for the separation of A B from C was that of fractional dialysis. Another method was based upon the use of uranium acetate[34] for the precipitation of C. Although most protein precipitates appear to adsorb the active principles, the use of uranium acetate appears to be the least objectionable. However, since these methods of attack are not used in our final method, we refrain from recording the hundreds of experiments that have been conducted in these directions.

Our final method involves the separation of B C from *A*. Although this first step may be partly accomplished by the use of effective protein precipitants such as tannic acid and phosphotungstic acid, the subsequent recovery, particularly from the phosphotungstate, requires rather heroic methods that might injure the active principles[40] and consequently we have used the more gentle process of salting out the proteins, together with the active principles, by means of salts such as sodium chloride or ammonium sulfate.

Salting-out Methods

Although Osborne and Vincent[41] had observed in 1900 that a part of the pressor activity of pituitary solutions is present in the salted-out fraction obtained by the addition of ammonium sulfate, no practical development resulted from this observation until 1913, when Clover[42] attempted to isolate the active principle by fractional precipitation by salting-out methods. Although mistaken in his conclusion that his potent salted-out fraction was an approximation of the active principle itself, Clover's work led to the first water-soluble pituitary preparations in solid, stable form.

[39] Dudley, J. *Pharmacol.*, 21, 111 (1923). isolated a considerable amount of creatinine from his extracts.

[40] Ref. 39, p. 104.

[41] Osborne and Vincent, Brit. Med. J., 1, 502 (1900).

[42] Clover, U. S. Patent Application of March 3, 1918; see No. 1,373,551.

Recently we have standardized by both pressor and oxytocic methods one of the best specimens of this "Proto-pituitrin," prepared by Clover in 1913, with the following results.

TABLE IV

Assay in *1913* *0.5* mg. per cc. yielded a pituitary extract equal to the *1913* standard
Assay in *1927* *0.5* mg. = 8.5 Oxytocic units
Assay in *1927* *0.5* mg. = *7.5* Pressor units

Two results are apparent: (1) this solid preparation remained stable for a period of fourteen years, and (2) the oxytocic and pressor activities are present approximately in the proportion in which they occur in the pituitary gland.

All of our work on products obtained by salting-out methods from relatively *concentrated* solutions has led to the conclusion that both principles are carried down into the precipitate in substantially the proportions in which they occur in the gland. Quite a different result is obtained in working with dilute solutions.

Comparison of the figures in Col. 1 of Table II with those in Col. 3 illustrates the completeness with which the activity is recovered by salting out in a fairly concentrated solution containing 50 to 100 units per cc. When relatively dilute solutions are treated with salt, a considerable loss of activity occurs, due to incomplete precipitation, as is illustrated by the following experiment.

One hundred cc. of a posterior lobe extract assaying *10* oxytocic units and *10* pressor units per cc. and containing 0.5% chloretone was treated with *30* g. of solid sodium chloride. The protein fraction together with the precipitated chloretone was removed with the centrifuge. The solution as well as the salted-out precipitate was then subjected to assay by both methods with the following result.

TABLE V

	No. of pressor units	No. of oxytocic units
Original solution	*1000*	*1000*
Salted-out fraction	*500*	*700*
Filtrate	*400*	*250*

The above results show not merely that dilute solutions are incompletely precipitated by salting-out methods, but also that the two activities are carried down with the protein fraction in unequal amounts. We have here another bit of evidence which disagrees with the theory that both types of activity are due to a single hormone.

The Separation of the Pituitary Hormones from Proteins: Separation of the Fraction B C into B and C

The hormones of the posterior lobe of the pituitary gland are not readily separated from foreign gland tissue and are carried along with the protein fractions. In this respect they resemble insulin and the parathyroid hormone rather than the simpler hormone, adrenaline. However, the method of manipulation of these protein extracts that has proven successful with insulin, namely, iso-electric precipitation, and which can be applied also to the purification of the parathyroid hormone, fails when applied to pituitary extracts. A new method of manipulation was required and has been devised.

After partial purification by salting out, the pituitary protein fraction is much more susceptible to fractionation than is the crude gland extract. However, the usual organic solvents used for such fractionation purposes, as for example alcohol, do not yield very satisfactory results.

An essential part of our method consists in the choice of an organic solvent which acts chemically with the active principles, due possibly to salt formation, and which acts simultaneously as a solvent for the salts of the active principles but is a relatively poor solvent for foreign protein material. An important prerequisite for such a solvent is that it must not injure the active principles.

The ideal solvents have been found in the aliphatic monocarboxylic acids of low molecular weight. Our work has been chiefly with acetic, propionic, and butyric acids, all of them being used in relatively high concentration and in the case of acetic acid in practically anhydrous form. The solvent action of propionic acid containing 5% of water and butyric acid containing about 10% of water is practically equivalent to 98–100% acetic acid. Since the results with acetic acid are highly satisfactory and since this solvent is also the cheapest one, the experiments to he described will deal with this particular acid.

The solution of the active principles in glacial acetic acid at room temperature (25°) is stable for days. After a month a perceptible loss of activity is observed, but in the following experiments the material need be exposed to the acid during only an hour. The advantages of such a method are in obvious contrast to methods involving reactive agents such as mercuric chloride and barium hydroxide.

The pituitary proteins are relatively insoluble in glacial acetic acid, whereas the active principles are readily extracted by this solvent. The amount of foreign protein extracted, however, is dependent upon the moisture content of the acid—for example, 98% acetic acid will extract appreciable quantities of protein, whereas 100% acetic acid will dissolve very little protein but it will extract the physiologically active compounds although with more difficulty than when the 98% acid is used. More dilute acid than 98% may be used as, for example, a solvent containing 10 to 20% (or even more) of water, but in this case the proteins and contaminating salt will dissolve completely and the subsequent fractionation by the addition of organic precipitants will be more tedious.

We find that the acetic acid extract may be subjected profitably to fractional precipitation by the gradual addition of acetone, ether, and petroleum ether in the order specified. When this is done, the first few fractions are found to be relatively inert, but successive fractions show an increasing potency. Acetone is the best precipitant for the inert proteins; subsequently the pressor principle, together with varying quantities of the oxytocic principle, is precipitated in a series of fractions by the addition of sulfuric ether, and finally complete precipitation is secured by the addition of a hydrocarbon precipitant such as petroleum ether.

By several repetitions of the fractionation process, it is possible to obtain the active principles in very potent form.

The steps involved in this concentration of the active principles and their separation are as follows:

(1) Extraction of the gland material according to the known method, using dilute aqueous acetic acid.

(2) Concentration of the dilute extract at a low temperature.

(3) Separation of the activity. together with proteins, by the addition of salt.

(4) Extraction of the salted-out fraction with glacial acetic acid.

(5) Fractionation of the acetic acid extract by the addition of organic liquids such as acetone, ether and petroleum ether.

The U. S. P. pituitary powder is prepared under special conditions[43,21] from pituitary glands collected within thirty minutes after the death of the animal. We have already designated the potency of this powder as 100%. In four preparations we were able twice to duplicate material possessing this potency, but two other lots, for some unexplained reason, possessed a potency of only 70%.

Commercial desiccated posterior lobe obviously is less potent than the standard powder and in actual practice a good technical product will test 40 to 60% of standard. A satisfactory method of separating the active principles, however, should be independent of the potency of the starting material and, indeed, we have found this to be true of the method to be described.

Experimental Procedure

(1) An aqueous extract of the posterior lobe of the pituitary gland is prepared by extracting 100 g. of the commercial acetone-desiccated gland material testing 50% of U. S. P. standard with 10 liters of 0.25% acetic acid. The mixture is gradually heated to a temperature of about 95° during a half-hour period, cooled quickly and then filtered to remove the insoluble gland residue, which is reextracted with one liter of the acidified water in order to secure a fairly complete extraction. The combined filtrates should contain 100,000 units of oxytocic activity and an equal number of units of pressor activity.

(2) The filtrate is then concentrated at a low temperature to a volume

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[43] *U. S. P.*, X, page 220.

of one liter. Since the active principles in acid solution are stable toward oxidation by air, evaporation with the aid of a current of warm air is permissible,

(3) The concentrated extract is treated with 550 g, of c. p. ammonium sulfate. The precipitate is filtered on a hardened filter paper, pressed, dried and powdered. The weight of salted-out product will be 20 to 40 g. according to the amount of salt present, an excess of which is not objectionable.

(4) The salted-out product is extracted with successive portions of glacial acetic acid (99–100%) a total volume of 500 cc. of acetic acid being used.[44] The amount of glacial acetic extracted material will be approximately 5 to 8 g., provided care is taken to prevent undue exposure to the moisture of the air during the extraction process.

(5) The acetic acid extract is now treated with 1250 cc. of sulfuric ether and then immediately with 2500 cc. of petroleum ether, which treatment precipitates the active material completely. The precipitate is filtered off by suction, washed with ether and dried. Its weight should be 5 to 10 g. varying with the water content of the acetic acid, and a potency test by both the pressor method and the oxytocic method should demonstrate the presence of 80 to 90% of the activity contained in the original 100 g. of desiccated gland material. Ninety to ninety-five per cent. of the inert material has thus been removed by our process up to this stage. Assay shows the product to possess a potency of 450 to 900% of standard according to the weight, the oxytocic and pressor activities being practically balanced.

The uniformity of this extraction and purification method is illustrated by the following four practical experiments conducted on a manufacturing scale.

TABLE VI

SEPARATION OF ACTIVE PRINCIPLES FROM INERT MATERIAL ON A MANUFACTURING SCALE

Expt. no.	No. of pressor units in desiccated gland	No. of oxytocic units in desiccated gland	No. of pressor units extracted	Yield of final product, g.	Potency by pressor test, %	Potency by oxytocic test, %
1	3,500,000	3,620,000	3,180,500	203	625	625
2	3,500,000	3,620,000	3,470,000	237	500	600
3	3,500,000	3,620,000	3,450,000	258	500	600
4	3,500,000	3,620,000	3,180,500	250	500	625

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[44] In order to secure an efficient extraction the following method may be applied. The salted-out product is divided into four equal part lots A, B, C and D. Part Lot A is extracted with seven times its weight of acid and this first extract set aside. A is then reextracted with a second portion of acid but this second extract is used for extraction of Part Lot B after which the second extract is combined with the first. In making the third extract Lots A, B and C are extracted in this respective order and the procedure is continued in this manner until each fraction has been extracted four times before being discarded and a total of seven portions of acetic acid have been used.

Partial Separation of the Two Active Principles

As a next step it is advantageous to remove a part of the oxytocic activity by the following simple process. A complete separation at this stage is not feasible because of the tendency of the protein fractions to adsorb the oxytocic fraction.

Five g. of the material assaying 500–900% of the U. S. P. powder is dissolved in 250 cc. of 98% acetic acid at a temperature of 40" and precipitated immediately by the addition of 2.5 volumes of sulfuric ether previously warmed to 30°. The flocculent precipitate is allowed to settle rapidly (not over five minutes) and is filtered by suction, washed with ether and dried.

The precipitate is immediately redissolved in 250 cc. of 98% acetic acid and precipitated as before. The recovered material will weigh 4.5 to 4.7 g.

The ether filtrate contains oxytocic activity together with traces of salts such as ammonium acetate. The active fraction may be precipitated by the addition of petroleum ether but the resultant solution is usually so difficult to filter that the following procedure is preferred.

The two ether-acetic filtrates (above) are combined and refiltered through hardened filter paper and the *clear* filtrate is treated with 10 cc. of water (which must dissolve completely) and two volumes (about **3** liters) of petroleum ether. A fine mist is thrown out which carries down practically all the oxytocic activity and usually collects as a varnish on the sides and bottom of the container after standing for several hours or overnight. The *clear* liquid is decanted and the gummy precipitate dissolved in 50 cc. of water and filtered free from fat. Based on solid content, this petroleum ether precipitate contains oxytocic material of a potency of 5000 to 12,000% and not more than 3–4% of pressor activity per 100% oxytocic activity.

The following practical result has been duplicated many times. Ten g. of a partially purified solid assaying 600% oxytocic and 500% pressor activity yielded by this process 9.6 g. of a fraction assaying 500% pressor but only 325–375% oxytocic activity. However, the petroleum ether precipitate, taken up in 100 cc. of water, had a solid content of 350 mg. and contained 50,000 to 60,000 units of oxytocic activity, thus accounting for the oxytocic activity removed from the precipitate. Such a solution is suitable for subsequent use in the purification of the oxytocic principle and also, after suitable dilution, for practical clinical use, since it contains only small amounts of pressor activity.

Fractionation of the Pressor Principle

(a) Five g. of partially separated material testing 500–900% by the pressor test but only approximately one-half this potency according to the oxytocic test, is dissolved in 100 cc. of 98% acetic acid at room temperature and the solution is filtered by suction from a small amount of salt and other insoluble impurities.

(b) To the filtrate is added 40 cc. of acetone. The precipitate, consisting mainly of protein containing only a small amount of active material, is filtered off, washed with ether and dried.

(c) The filtrate from (b) is treated with an additional 40 cc, of acetone and a second protein fraction is obtained as before, although this fraction contains a slightly more active material.

(d) The filtrate from (c) is treated with about 25 cc. of sulfuric ether and the precipitate filtered off and dried as before. This fraction is more potent than (c) by both the pressor and oxytocic tests.

(e) The filtrate from (d) is treated with 125 cc. of ether and the precipitate filtered off and dried. This fraction is very active by the pressor test but less active by the oxytocic test, thus plainly showing a separation of the active principles.

(f) The filtrate from (e) is treated with an excess (about 500 cc.) of sulfuric ether in order to precipitate the remainder of the pressor activity.

(g) The filtrate from (f) contains only a trace of pressor activity but contains the bulk of the oxytocic activity. The latter may be obtained by the addition of petroleum ether as already described. Due to the presence of moisture this fraction may precipitate as a gummy mass but can be obtained in the form of a white solid by dissolving in absolute alcohol and precipitating with an excess of ether. If it precipitates as a liquid it must be concentrated at a low temperature.

The results obtained by this fractionation method are shown in the following experiment selected at random from a large number of similar results.

Thirty g. of material assaying 750% by pressor and 375% by oxytocic test was treated with 600 cc. of 98% acetic acid and fractionated with the following results.

TABLE VII

FRACTIONATION OF PRESSOR PRINCIPLE AND SEPARATION OF A POTENT OXYTOCIC FRACTION

Fraction number	Amount and kind of solvent added	Assay of fraction. %	Weight of fraction, g.
1	Acetic acid	Practically inert	5.4
2	225 cc. Acetone	300 Pressor, 150 oxytocic	7.7
3	225 cc. Acetone	400 Pressor, 200 oxytocic	8.4
4	150 cc. Ether	750 Pressor, 250 oxytocic	1.9
5	750 cc. Ether	3125 Pressor, 700 oxytocic	4.2
6	4000 cc. Ether	1875 Pressor, 1625 oxytocic	1.0
7	Petroleum Ether	120 Pressor, 5000 oxytocic	0.8
		Total	29.4

In the above experiment 220,000 pressor units were recovered from a total of 225,000 and likewise 100,000 oxytocic units from a total of 122,000 shown by the initial assay.

Examination of the above table shows that fractions 2, 3 and 4 are relatively weak. They consist chiefly of protein material which naturally carries along an appreciable amount of activity. However, a separation and concentration of the two activities is taking place as is shown by the fact that fraction four is three times as potent by pressor as by oxytocic test, and the large fraction, five, is more than four times as potent by pressor as by oxytocic test. The oxytocic activity is accumulating in the residual solution and it is therefore to be expected that the last solid fraction (No. 6) will be comparatively potent in oxytocic activity also, since the oxytocic principle is not very soluble in ether.

Refractionation and Further Concentration of the Pressor Principle

The more potent of the separated fractions may be further concentrated by a repetition of the process already described, applying the same to the individual fractions.

The following laboratory experiment illustrates the results obtained in actual practice.

Seven g. of material assaying 3125% by pressor test and 700% by oxytocic test (equivalent to Fraction 5, Table VII) were dissolved in 210 cc. of 98% acetic acid and refractionated with the following results.

TABLE VIII

FRACTIONATION OF THE PRESSOR PRINCIPLE

Fraction number	Amount and kind of precipitant added	Assay results. %	Weights of fraction, g.
1	210 cc. Acetone	1000 Pressor, 150 oxytocic	1.35
2	105 cc. Acetone	1625 Pressor, 400 oxytocic	0.95
3	75 cc. Ether	3000 Pressor, 500 oxytocic	1.15
4	300 cc. Ether	4000 Pressor, 750 oxytocic	2.40
5	600 cc. Ether	2500 Pressor, 2000 oxytocic	0.52
6	Filtrate	150 Pressor, 4000 oxytocic	0.25
		Total	6.62

Repeated fractionation of the 4000% pressor fraction yields a fraction testing 6250% but it is difficult to increase the potency beyond this figure by this method. The subsequent use of other solvents, such as the alcohols, has raised its potency only to 8000%. This product is now being subjected to various purification methods in the hope of obtaining it in a condition of maximum potency.

The distribution of the pressor hormone among the various fractions in this process is shown graphically in Fig. 1, which is based upon the refractionation of 46.5 g. of a partially separated product testing 750% by pressor and 375% by oxytocic tests. The dark areas represent the amount of pressor principle present in the respective fractions, assuming a potency of 7500%, a value which we already know is somewhat below the actual potency of the pure principle. The white areas represent inert material.

Results analogous to those illustrated in Series 2 have already been recorded in Table VII. The best Fraction, 2E, testing 3125%, was refractionated and yielded Fractions 3A, 3B, 3C, 3D and 3E, testing 1000, 1625, 3000, 4000 and 2500%, respectively. The latter results are recorded in Table VIII.

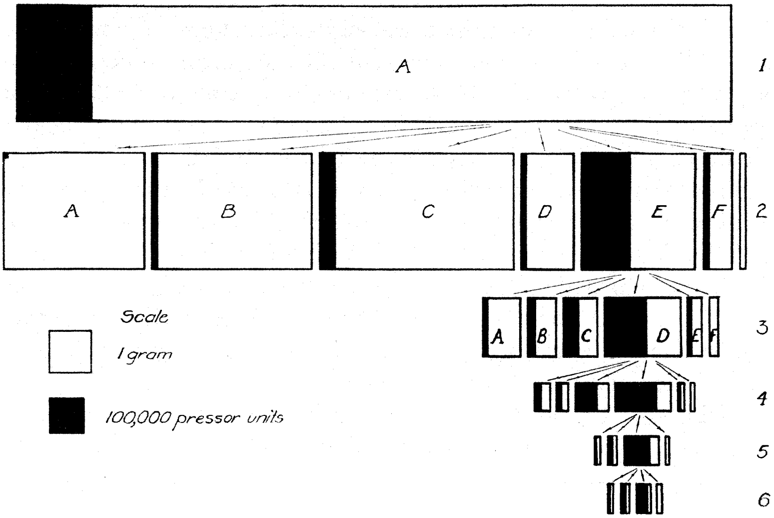

Fig. 1.—Separation of the pressor principle.

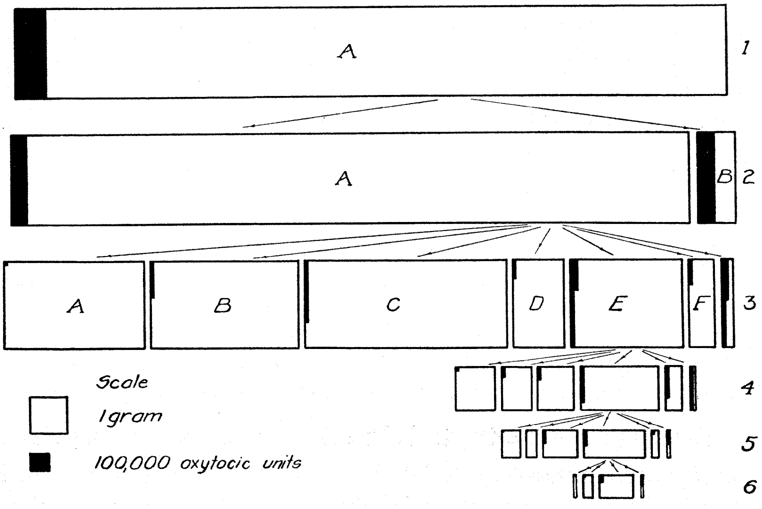

Fig. 2.—Separation of the oxytocic principle.

Fraction 3D, testing 4000%, was refractionated and yielded Fractions 4C and 4D, both testing 5000%. The latter fraction yielded a large

Fraction 5C, testing 5000%, and refractionation of this yielded the Fractions of the 6 series, the most potent of which tested 6250%.

The distribution of the oxytocic hormone among the various fractions in the process that has been described in detail is shown graphically in Fig. 2, which is partly based upon the oxytocic values recorded in Tables VII and VIII. The dark areas represent the amount of oxytocic principle present in the respective fractions, assuming a potency of 20,000% for the pure principle, an estimate which is, no doubt, considerably below the actual value. The white areas represent inert material.

The separation shown in Series 2, Fractions A and B, corresponds to the results obtainable by the procedure described above under the section headed "Partial Separation of the Two Active Principles." The fractions in Series 3 are identical with the fractions in Series 2 of Fig. 1; for example, Fraction 2E of Fig. 1 and 3E of Fig. 2 are based upon the same fraction, the former chart illustrating the proportion of pressor principle and the latter chart the amount of oxytocic principle in this sample.

It is to be noted that the oxytocic activity tends to accumulate in the end fractions shown at the right-hand end of the chart.

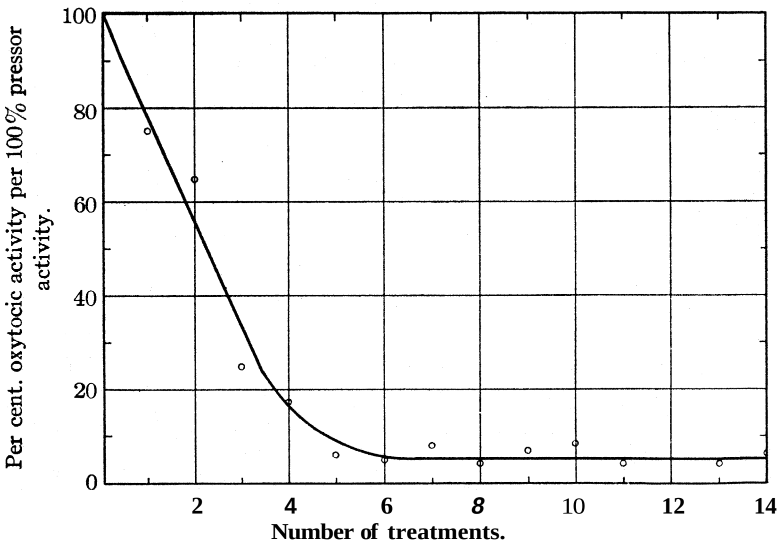

Fig. 3.—Separation of oxytocic principle from the pressor principle.

Limits of Separation of the Oxytocic Principle from the Pressor Principle

The most potent pressor material obtained by the acetic acid fractionation method, namely, a product testing 6250%, still contains approximately 10% of oxytocic activity per 100% pressor activity. It is difficult to reduce the oxytocic activity below 4% per 100% pressor. This is illustrated in Fig. 3, which represents fourteen treatments aiming at the removal of the oxytocic activity by the method already described, namely, solution in glacial acetic acid and precipitation with ether.

The curve illustrates the fact that the oxytocic activity is rapidly removed in connection with the first four treatments with acetic acid. After the sixth treatment the amount of oxytocic activity remains almost constant.

These results suggest that a small amount of oxytocic activity may be inherent in the pressor principle itself and we have in progress a new series of experiments aiming at a solution of this interesting problem. The fact that the pressor principle, as such, may possess a slight stimulating effect on smooth muscle would not be an unique case, since some relatively simple substances (as for example tyramine) also show both types of activity.

Purification of the Oxytocic Principle

The oxytocic principle resembles the pressor principle in every way except that it is appreciably soluble in organic solvents and particularly in a mixture of ether and acetic acid. A practical method of obtaining a potent solution of the oxytocic principle has already been described in the above experimental procedure under the heading "Partial Separation of the Two Active Principles."

The ether-acetic acid solution of the oxytocic fraction may be evaporated to dryness at a low temperature and the residue taken up in 0.25% acetic acid and filtered. This acid extract is then assayed for total solids and for oxytocic activity and usually tests 5000% of U. S. P. standard. Precipitation of the ether solution by the addition of petroleum ether according to the methods already described yields a product testing up to 12,000%, which is relatively low in pressor activity, and this method is preferable. The gummy precipitate is then merely dissolved in 0.25% acetic acid.

The aqueous solution containing the oxytocic fraction as the acetate may be evaporated at a low temperature. The residue is treated with alcoholic tartaric acid, which dissolves the active substance but may leave a crystalline residue of ammonium acid tartrate which is filtered off. From the alcoholic solution the oxytocic tartrate may be fractionally precipitated by the addition of ether. This process, however, has not raised its potency beyond 15,000–20,000%, and a more satisfactory method of purification is being sought.

Assay of such a fraction by the pressor method indicates that 98 to 99% of the pressor activity of the gland has been removed. Apparently there is little difficulty in removing the pressor from the oxytocic principle, and even for practical clinical work we have been able to supply a product which assays only 4% pressor for each 100% by oxytocic assay.

Adrenaline, which is an amine, may be precipitated from aqueous solutions of its salts, when present in sufficient concentration, by neutralization with ammonia. The pituitary hormones also appear to be amines but they are not precipitated from aqueous solutions of their salts upon neutralization, since the bases themselves are extremely soluble in water. Further work on the purification of these products will appear in subsequent articles.

Conclusive Evidence of the Presence of Two Principles

The evidence that we have presented in the quantitative results reported above should leave little doubt that at least two principles are present in pituitary extracts and that these two principles may be separated by practical methods. It seems advisable, however, to demonstrate that in our process none of the activity has been injured or one product converted into another. In other words, the sum of the parts should make a whole; and this should be demonstrated not merely by adding up the separate assay results but also by synthesis of the original by recombining the parts. This has been done in the following experiment.

A sample of a partially purified product was found to test **625%** by both the oxytocic and pressor methods (see Table VI, Expt. **1).** Ten g. of this material was then subjected to the acetic acid fractionation method with the following results.

TABLE IX

INITIAL FRACTION OF A PURIFIED PRODUCT CONTAINING ACTIVITIES IN ORIGINAL PROPORTIONS

Fraction	Wt., g.	Oxytocic assay, %	Pressor assay, %	Oxytocic units	Pressor units
1	3.8	175	125	13,300	9500
2	2.75	200	200	11,000	11,000
3	1.2	300	400	7200	9600
4	1.55	1875	2500	58,000	77,500
6	0.28	6000	500	33,600	2800
6	8 liters filtrate	..	...	2500	2500

Fractions **1** and **2** were obtained by acetone precipitation, Fractions **3** and **4** by ether precipitation and Fraction **5** with the aid of petroleum ether. Note that Fraction 1 contains more oxytocic than pressor activity, but in **3** and 4 the pressor activity is in excess, whereas in Fraction **5** the oxytocic activity is again in great excess. The large volume of filtrate contained only **2%** of the total activity.

The initial material used in this experiment contained **125.000** oxytocic units and **125,000** pressor units. The assays of the separate fractions total up to **125,600** oxytocic units and **113,100** pressor units.

The fractions were then recombined and the resultant mixture was submitted to assay as an unknown. The resultant pituitary product on the basis of the physiological tests was indistinguishable from the original product and assay demonstrated it to test **575%** by pressor test and **625%** by oxytocic test. This represents **110,400** pressor units and **120,000** oxytocic units, results which are within the limits of experimental error.

The above experiment has been repeated using known quantities of highly purified oxytocic and pressor fractions. Such solutions when combined in theoretical proportions were indistinguishable pharmacologically from plain pituitary extracts. Incidentally, these tests show that the oxytocic assay is not influenced seriously by the presence of the pressor principle and, *vice versa,* the pressor assay method is not adversely affected by the presence of moderate amounts of the oxytocic principle. The effect of the presence of excessive amounts of one principle upon the assay of the other requires further study.

The Diuretic-Antidiuretic Principle Appears to be Identical with the Pressor Principle

Extracts of the posterior lobe of the pituitary have a diuretic-antidiuretic action. Under some conditions injection of such extracts causes diminished excretion of urine but under different conditions the flow of urine is markedly increased.

We were interested in finding out which of the active principles, the oxytocic principle or the pressor principle, has the diuretic-antidiuretic action. In order to determine this question extracts containing the two activities were tested on rabbits.

The method of experiment was similar to that used by Magnus and Schafer,[45] Schäfer and Herrington,[46] and Houghton and Merrill[47] on dogs; and more recently on rabbits by Abel, Rouiller and Geiling,[2] Mackersie,[48] Smith and McClosky,[49] and others.

The rate of flow of urine was observed by counting the number of drops in five-minute intervals falling from a cannula tied into the urinary bladder. The rabbits were anesthetized with urethan (ethyl carbamate), *2* g. per kilogram of body weight, given by subcutaneous injection. The cannulas used were funnel-shaped at the end which was tied into the bladder and obliquely pointed at the other end. They were 1 cm. in diameter so as to prevent the possibility of capillary action interfering with the free flow of urine. In making a test the rabbit was laid on a board so that the cannula extended vertically downward through a hole in the board. Rabbit and cannula being in this position permitted the urine to drop as fast as it entered the bladder without the possibility of pocketing.

The solutions used for the diuresis experiments were Pituitrin which tested 100% pressor and 100% oxytocic, a solution of the pressor fraction which tested 100% pressor and 8% oxytocic; and a solution of the oxytocic fraction which tested 100% oxytocic and 4% pressor.

A typical experiment showing the effect of intravenous injections of Pituitrin, pressor fraction and oxytocic fraction is illustrated in Fig. *4.* These three substances were used in rotation so as to compare their effects on the same rabbit. The dosage of Pituitrin is stated in International Units, the dosage of the oxytocic fraction is stated in units equal to the International Units, and the dosage of the pressor fraction is stated in units of the pressor activity which we have defined above. The rabbit weighed 2.1 kilograms and had been fed on oats and green food with water always accessible.

It will be noted that Pituitrin and the pressor fraction caused a marked increase in the flow of urine while the oxytocic fraction caused only a slight increase in the flow. This difference is even more noticeable in some of

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[45] Magnus and Schafer, J. *Physiol*, *27,* Proc. ix *(1901).*

[46] Schäfer and Herrington, *Proc. Roy. Soc. (London),*77B, *571 (1906); Phil. Trans. Roy. Soc.,* 199B, *1 (1908).*

[47] Houghton and Merrill, J. *Am. Med. Assocn.,* 51,1849 *(1908).*

[48] Mackersie, *J. Pharmacol.,* 24, 83 *(1924).*

[49] Smith and McClosky, *ibid., 24,371 (1924).*

our other experiments. In only one experiment has there been any great flow of urine following the injection of the oxytocic fraction. It seems probable in that exceptional experiment some source of experimental error changed the apparent outcome. These diuresis experiments are still in progress and will be reported more in detail later by Dr. E. P. Bugbee.

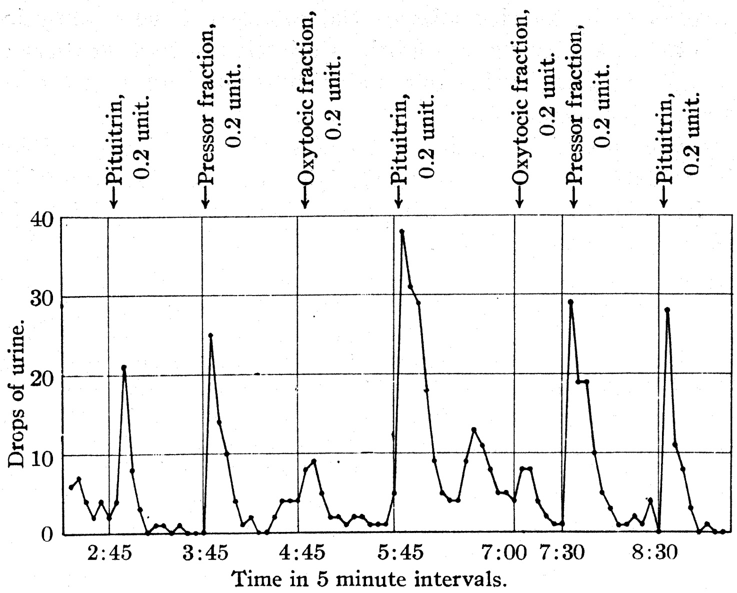

Fig. 4.—Showing the diuretic-antidiuretic effect of intravenous injections of pituitary extracts on a rabbit under urethan anesthesia.

The Pressor Effect of the Pressor Hormone

We have repeated the historical experiments of Howell[5] and of Schafer and Vincent[12] who have shown that when doses of pituitary extracts are administered intravenously in fairly rapid succession and in relatively large amounts a tolerance is quickly established so that after the second or third injection no further pressor effect is demonstrable.

When plain pituitary extracts are used the typical rise in pressure may actually be replaced by a depressor action due either to the presence of traces of histamine or to the acidity. Abel[50] has demonstrated this depressor action even with his purified fraction.

In repeating this early work we have used a purified pressor fraction and find that it acts exactly like an unmanipulated pituitary extract in respect to the development of tolerance, thus showing that the product has not been modified. However, the successive large doses fail to give

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[50] **Abel,** Rouiller and Geiling, **J.** Pharmacol., 22,303 **(1923).**

any depressor action, thus attesting to the degree of purification of the product. The details of this work will appear in a separate publication by Mr. L. W. Rowe.

Therapeutic Indications

In an article presented from the standpoint of the chemist it is naturally inadvisable to discuss in any great detail the medical aspects of this problem. However, in view of the fact that many of our readers may be interested in the possible applications of these hormones, the subject of therapeutic indication will be commented upon briefly.

The oxytocic principle seems indicated in those obstetrical cases where the physician wishes to avoid elevating a blood pressure that is already too high. Incidentally there is a possibility that this principle will yield more satisfactory and uniform oxytocic results when administered by itself than when mixed with the pressor hormone.

There is a strong probability that the pressor principle is the active principle which is of value in the treatment of diabetes insipidus, and preliminary clinical reports seem to confirm this opinion.

Pituitary extracts have not proved successful for the relief of asthmatic conditions. It has been suggested that the beneficial effects produced by one principle are neutralized by the unfavorable actions of the other. Obviously such practical questions can now be studied in a more scientific manner since the shotgun is replaced by the rifle.

In view of the fact that the two separated principles are available for study it is now possible for the physiologist and the pharmacologist to analyze more correctly the physiological responses caused by the administration of pituitary extracts.

General Discussion

We have no doubt that most of the previous investigators in this field have actually been working with partial separations of the active principles.

The simple operation of desiccating fairly fresh pituitary glands with acetone results in yielding a very crude extract which contains 8% of the total oxytocic activity and only 2% of the pressor activity. Investigators who have made aqueous or saline extracts without using acid have dealt with material deficient in pressor activity, but in general this fact was not realized because the deficient extracts were used as standards of comparison.

Abel[50] was convinced that his methods yielded all the various activities in the identical proportions present in the original gland material but upon repeating his work we were surprised to obtain in the first step involving the mercuric chloride treatment a yield of only 30% of pressor activity. This experiment was checked three times with almost identical results. In the light of our present work we repeated such an experiment and found the yield of oxytocic activity to be 60% and that of pressor activity to be 30% of the total amount originally present. It is evident, therefore, that the very first step in Dr. Abel's process involves a partial separation of the two principles.

The products that we have obtained by the processes described in the experimental part of this paper, in sufficient detail so that the results may be readily duplicated, are certainly close approximations to the active principles themselves. Although we feel that additional purification may raise the potency values above those reported here and that ultimately we or others will be able to secure these two principles in crystalline form, such purification is not essential to the successful clinical application of these two new products.[51]

In contrast to all previous workers in this field we are able not merely to obtain fractions differing from each other when subjected to the two acceptable quantitative assay methods (which result might be due to partial injury of a single principle), but we have been able to secure the following results which we believe are new.

(1) Complete quantitative evidence has been obtained proving that a separation may be effected and by recombining the fractions in the original proportions a pituitary solution indistinguishable from the original is again obtained, thus proving that no injury of any active principle has taken place.

(2) By continuing our fractionation process we have effected a separation of the two principles which for all practical purposes may be considered as complete.

(3) Both principles have been obtained in the form of stable, highly potent, water-soluble powders.

(4) The separated principles have for the first time been made available to the medical profession for experimental clinical use and thousands of ampoules of the purified separated products have been distributed for this purpose.

Summary

1. The posterior lobe of the pituitary gland contains two important active principles: one which raises blood pressure and another which stimulates contraction of uterine muscle.

2. A substantially complete separation of these two active principles has been accomplished by the employment of salting-out methods and, subsequently, by the use of appropriate solvents and precipitants.

3. Solutions of these separated active principles have been recombined

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[51] Note: This is analogous to the Insulin case. This product has proved to be a successful remedial agent and although recently it was obtained in somewhat more potent form and also in crystalline condition, it is not likely that the clinical use of Insulin will be greatly influenced.

to form a pituitary extract identical with the original from which they were prepared, thus proving that no decomposition **has** taken place.

4. The substantially pure pressor principle (β-hypophamine) has been obtained in the form of a white, stable, water-soluble powder 80 times as potent as the International Standard Powdered Pituitary.

5. The separated oxytocic principle (a-hypophamine) has been obtained in the form of a white, stable, water-soluble powder which is more than 150 times as potent as the International Standard Powdered Pituitary.

6. The pressor principle has been shown to be responsible for the diuretic-antidiuretic action of pituitary extracts.

7. The pressor principle when tested on animals for demonstration of pressor effects shows the development of tolerance which is characteristic of active pituitary extracts. It has been shown to possess no appreciable depressor action.

8. Both active principles are basic bodies, presumably amines.

9. Practical manufacturing methods have been developed for the separation of these two hormones and they have been made available to the medical profession for careful clinical trial.

10. As a result of this preliminary work the foundation is now laid for an investigation of the chemical nature of the separated hormones of the posterior lobe of the pituitary gland, together with a more exhaustive study of their pharmacological properties.

DETROIT, MICHIGAN

NEW BOOKS

General Chemistry. A Cultural Course Based upon the Texts of the Late Alexander Smith. By JAMES KENDALL, Professor of Chemistry, Washington Square College, New York University. The Century Company, 353 Fourth Avenue, New York City, 1927. xxix + 676 pp. 170 figs. and several plates. 13.5 × 20.5 cm. Price $3.50.

In this text Dr. Kendall has presented what he calls a cultural course in chemistry. It must be said, however, that if beginning students in chemistry master this book they will be entirely prepared to take advanced courses; hence it can be applied to any college or university freshman course with profit.

A number of additions to the usual content of the Smith texts have helped make the book interesting. The illustrations scattered liberally through it are very well chosen. This applies not only to those showing commercial processes but to the personal portraits of eminent chemists as well. The discussion of the personalities of these chemists is one of the ways in which human interest is aroused.

Familiar notes by Kendall add much to the ease of understanding of such topics as catalysis, ionization, etc. The citation of articles which may he assigned for reading is stimulating to the teacher at least. The new chapters on radium, atomic energy and atomic structure are also a distinct advance.

The writer feels sorry that Dr. Kendall has not seen fit to break away from the old idea of ionization and to give us a development based on the more modern ideas which he has included in the text. If the old ideas have been sadly shaken, and most chemists will agree that this is so, why wait for a perfect theory instead of stating logically the present accepted position? Such a revision would, of course, require a recasting of the methods for presenting the theory of ionization. That no one else has done this does not mean that it would not be acceptable. The book is in general up to the high standard of the Smith texts.

P. A. BOND

Leçons de Chimie Physique. (Textbook of Physical Chemistry.) By P. MAURICE VÈZES, Professor of Chemistry at the University of Bordeaux. Preface by G. Urbain. Librairie Vuibert, Boulevard Saint-Germain, 63, Paris, France, 1927. ix + 545 pp. 293 figs. 16.5 × 25.5 cm. Price (unbound) 50 fr.

The present work by a well-known authority on the platinum group of metals presents with clarity the principles of the classical physical chemistry. It is divided into four parts: the first consisting of four chapters treats Atoms and Molecules, their fundamental laws and the determination of atomic and molecular weights by the various methods. The second part is devoted to Electrochemistry with chapters on Electrolytes, Transport of Ions, Electromotive Force, Electrolysis and the Energy of Piles. The final chapter (IX) of Part Two introduces the atomic conception of electricity and modern atomic structure. (By a somewhat astonishing feat, the author was able to introduce and discuss many of the principles of *Radioactivity* without any mention of his distinguished countrymen whose names are universally associated with that subject.) Part III deals with Velocity of Reactions and Part IV with Chemical Equilibria.

The preface by Professor Urbain contains interesting comments on the teaching of Physical Chemistry, its relation to General Chemistry (between the two he makes a sharp distinction, rather from the didactic standpoint) and the value of Thermodynamics. The treatment of the latter is not segregated as in some texts, but distributed under various topics as occasion arises for its application.

S. C. LIND

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THIRTY-FOURTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1927

BY GREGORY PAUL BAXTER

RECEIVED FEBRUARY 6, 1928 PUBLISHED MARCH 7, 1928

The Annual Report of the German Committee on Atomic Weights appeared as usual.[1] Nearly all the following investigations appeared during 1927.

Boron.—Briscoe, Robinson and Smith[2] by means of a standardized float have determined the densities of three specimens of boron trichloride obtained from different sources and have found an extreme variation in the atomic weight of boron of 0.023 unit. Fractionation of two of these samples showed them to be impure and halved the extreme difference. There is no proof that further purification would not have removed the discrepancy entirely.

Carbon.—Sameshima[3] has determined the density and compressibility of acetylene.

TABLE I

DENSITY OF ACETYLENE, 0°

Pressure	Volume	Density	PV ($(PV)_1 = 1$)
0.5341	143.422	0.6241	1.0053
.6279	143.424	.7348	1.0038
.9988	143.431	1.1739	0.9995
1.0007	143.431	1.1749	1.0005
1.5096	143.441	1.7845	0.9938

By interpolation the normal density is 1.1747 and by extrapolation the limiting density 1.1615. Then $C_2H_2 = 26.03$ and $C = 12.005$.

Stock and Ritter[4] have compared oxygen and ethylene in a gas displacement balance and find the weight of the normal liter of ethylene to be 1.26057 and the deviation from Boyle's Law 1.00790. Using 22.415 as the gram molecular volume, the molecular weight of ethylene is 28.034 and the atomic weight of carbon is 12.001.

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[1] *Ber.*, **60B**, 1 (1927).

[2] Briscoe, Robinson and Smith, *J. Chem. Soc.*, 1927, 282.

[3] Sameshima, *Bull. Chem. Soc. Japan*, **1**, 41 (1926).

[4] Stock and Ritter, *Z. physik. Chem.*, **124**, 204 (1926).

Nitrogen.—Moles[5] discusses critically earlier work on the density and compressibility of ammonia and comes to the conclusion that 0.7715 and 1.01534 represent the most probable values of the density and compressibility, respectively. From these figures the atomic weight of nitrogen may be calculated to be 14.008.

Moles[6] reviews the evidence concerning the densities and compressibilities of oxygen and nitrogen and arrives at the following most probable values.

	Density	$(PV)_0/(PV)_1$	At. wt.	Gram molecular vol.
Oxygen	1.42892	1.00091	16.000	22.4148
Nitrogen	1 25046	1.00042	14.0082	.....

Moles and Clavera[7] have redetermined the density of nitrogen prepared by (1) decomposition of ammonium nitrite, (2) reduction of nitric oxide, (3) decomposition of urea by hypobromite, (4) decomposition of urea by sodium nitrite.

TABLE II

DENSITY OF NITROGEN

Method of prep.	Globe 3 455.18 ml.	Globe B, 580.49 ml.	Globe N_1, 585.09 ml	Globe N_3, 772 393 ml	Average
		Preliminary Series			
1	1.24989		1.25063		1.25026
1	1.25068		1.25113		1.25090
1	1.25005		1.25122		1.25083
1	1.25016				1.25016
				Average	1.25049
		Final Series			
1	1,25040	1.25042			1.25041
1	1.25018	1.25042			1.25030
1	1.25094	1.25068			1.25081
1	1 25042	1.25048			1.25045
1	1.25018	1.25045			1.25032
1	1.25049	1.25052			1.25051
1	1.25124	1.25044			1.25084
1	1.25054	1.25057			1 25056
				Average	1 25052
2	1.25055	1.25059			1.25057
2	1,25059	1.25066			1.25062
2	1 25041	1.25051			1.25047
2	1.25030	1.25039			1.25034
				Average	1.25049
3	1.25052				1.25052
3	1.25026	1.25037			1.25032
3	1.25045	1 25076			1.25061
				Average	1.25046

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[5] Moles, *Anales soc. españ. fís. quím.*, 24, 717 (1926).

[6] Moles, *Z. anorg. allgem. Chem.*, **167,** 40 (1927).

[7] Moles and Clavera, *ibid.*, 167, 49 (1927).

TABLE II (*Concluded*)

Method of prep.	**Globe 3** 466.18 ml.	Globe B, 680.49 ml.	Globe N_1, 685.09 ml.	Globe N_3 772.393 ml.	Average
4	1.25074				1.25074
4	1.25025				1.25025
4	1.25075				1.25075
4	1.26018				1.25018
4	1.25060			1.25057	1.25059
4	1.25052			1.25039	1.25046
4	1.25054			1.25028	1.25041
				Average	1.25048
Average	1.25050[a]	1.25052	1.25096	1.25041	1 25050[a]

[a] Omitting preliminary series.

New determinations of the deviation from Boyle's Law made by **Batuecas** are presented.

	$(PV)_0/(PV)_1$
	1.00059
	1.00025
	1.00076
	1.00021
	1.00050
Average	1 00046

By combining the experimental averages for density and compressibility with the value for normal molecular volume, 22.4148, the atomic weight of nitrogen is computed to be 14.008.

Neon.—Baxter and Starkweather[8] have redetermined the density and

TABLE III

THE DENSITY OF NEON

0°. g = 980.616

Sample	No. of adsorptions	Globe IV, 2110.95 ml.	Globe VII, 2117.77 ml.	Average
		P = 760 mm.		
1	7		0.89991	
1	9		.89988	
1	11		.89987	
		Average	.89989	
2	23		.89992	
2	27		.89990	
		Average	.89991	
1 + 2	13 and 29	0.89991	.89994	0.89993
1 + 2	15 and 31	.89987	.89996	.89992
1 + 2	17 and 33	.89988	.89991	.89990
1 + 2	18 and 34	,89981	.89990	.89986
1 + 2	19 and 35	.89993	.89992	.89993
1 + 2	20 and 36	.89984	.89997	.89992
	Average	.89987	.89993	.89991
			Average of all	0.89990

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[8] Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, **14**, 50 (1928).

TABLE III (*Concluded*)

Sample	No. of adsorptions	Globe IV, 2110.95 ml.	Globe VII, 2117.77 ml.	Average
P = 506.667 mm.				
1	9		0.60000	0.60000
1 + 2	13 and 29	0.60000	.60007	.60004
1 + 2	17 and 33	.60007	.60010	.60009
1 + 2	18 and 34	,60002	,60014	.60008
1 + 2	21 and 37	.59999	,60006	.60003
1 + 2	22 and 38	.59998	.60006	.60002
	Average	.60001	,60007	,60004
P = 253.333 mm.				
1	11	0 30000	0.30007	0.30004
1 + 2	15 and 31	.30007	,30009	.30008
1 + 2	19 and 35	.30003	,30010	.30007
1 + 2	20 and 36	.30009	.30018	.30014
1 + 2	21 and 37	.30012	,30010	.30011
1 + 2	22 and 38	.30011	,30012	,30012
	Average	.30007	30011	,30009

compressibility of neon which had been purified both chemically and by adsorption on chilled, dehydrated chabazite until spectroscopically free from helium and nitrogen.

The deviation from Boyle's Law is calculated in the conventional way from the densities at different pressures to be 0.99942 and the atomic weight of neon 20.182.

Chlorine.—E. Gleditsch and L. Gleditsch[9] have compared the densities of solutions of sodium chloride, saturated at 18°, prepared from salt occurring at different levels in the Alsatian deposits. Since no difference greater than the experimental error was found, the isotopic composition of the chlorine must be the same.

Source	Density of saturated solution
Ordinary (marine)	1,201066
Alsation, Level 1 (highest)	1.201063
Level 2	1.201076
Level 3	1.201070
Level 4 (lowest)	1.201058

Honigschmid, Chan and Birckenbach[10] purified chlorine by distillation and collected the product in exhausted glass bulbs which were ultimately sealed. These were weighed in air and in water, and were broken under a solution of ammonium arsenite. The glass fragments were collected and weighed. Comparison with silver followed and the silver choride was collected and weighed. The change in weight on fusion in chlorine and in air was applied as a correction. Ag = 107.880. Weights are in vacuum.

[9] Gleditsch and Gleditsch, J. *chim. phys.*, 24, 238 (1927).

[10] Honigschmid, Chan and Birckenbach, *Z. anorg. allgem. Chem.*, 163, 313 (1927).

TABLE IV

ATOMIC WEIGHT OF CHLORINE

Wt. of Cl	Wt. of Ag	Ratio Cl:Ag	At. wt. of Cl	Wt. of AgCl	Ratio Cl:AgCl	At. wt. of Cl
Preliminary Series—Commercial Chlorine						
1.59759	4.86100	0.328655	35.455	.....	. .	
1.85886	5.65594	.328656	35.456	7.51482	0.247359	35.455
1.79223	5.45306	.328665	35.456	7.24567	,247352	35.454
1.37498	4.18367	.328654	35.455	5.55893	247346	35.453
1.40453	4.27340	.328668	35.457	5.67813	.247358	35.455
	Average	.328660	35.456		247354	35.454
Final Series—Chlorine from $KMnO_4$ + HCl						
2.85458	8.68543	0.328663	35.456	11.54006	0.247363	35.456
2.25569	6.86312	.328668	35.457	9.11885	.247366	35.457
2.38732	7.26367	.328666	35.457	.....	.....	....
2.46049	7.48635	.328664	35.457	9.94697	.247361	35.456
3.35955	10.22139	,328678	35.458	13.58097	.247372	35.458
2.96007	9.00620	.328671	35.457	11.96628	.247368	35.457
2.21357	6.73502	,328666	35.457	8.94856	.247366	35.457
3.04333	9.25949	.328671	35.457	12.30283	.247368	35.457
2.17711	6.62409	,328666	35.457	8.80126	.247363	35.456
	Average	.328668	35 457		,247366	35.457

In another series of experiments silver chloride was synthesized from weighed amounts of silver and hydrochloric acid from different sources. Sample Ia was prepared from ordinary hydrochloric acid by distillation

TABLE V

ATOMIC WEIGHT OF CHLORINE

Sample	Wt. of Ag	Wt. of AgCl	Ratio AgCl:Ag	At. wt. of Cl
Ia	4.29967	5.71283	1.32867	35.457
	4.29980	5.71285	1.32863	35.453
	4.29979	5.71309	1.32869	35.459
	4.29969	5.71291	1,32868	35.458
		Average	1.32867	35.457
Ib	5.46510	7.26138	1,32868	35.458
	4.29656	5.70869	1.32867	35.456
	5.60428	7.44636	1,32869	35.459
	7.05748	9.37695	1.32866	35.455
		Average	1.32867	35.457
II	4.66452	6.19769	1,32869	35.459
	4.70792	6.25510	1,32863	35.453
	5.24426	6,96804	1,32870	35.460
	4.95507	6.58374	1.32869	35.459
	4.77530	6.34466	1.32864	35.454
	6.58505	8.74935	1,32867	35.457
		Average	1.32867	35.457
III	5.56529	7,39451	1.32868	35.458
	5.07732	6.74608	1.32867	35.457
		Average	1.32867	35.457

after removing bromine and iodine. To prepare Sample Ib sodium chloride was crystallized and converted to hydrogen chloride. The solution of the latter was purified as above. Samples II and III were prepared from extreme fractions of carbon tetrachloride which had been repeatedly fractionally distilled with the object of separating the chlorine isotopes. Weights are in vacuum. Ag = 107.880.

The atomic weight of chlorine obtained as the result of these experiments is identical with that found by Richards and Wells.

Scandium.—Smith[11] purified scandium material (1) by solution of the fluoride in ammonium fluoride and (2) by purification of the double ammonium tartrate. The oxide was prepared through the oxalate and was converted to chloride in a current of nitrogen and carbon tetrachloride in an enclosed bottling apparatus. The chloride was then compared with silver. Weights are in vacuum. Cl = 35.457.

TABLE VI

ATOMIC WEIGHT OF SCANDIUM

Sample	Weight of $ScCl_3$	Weight of Ag	Ratio $ScCl_3:3Ag$	Atomic weight of Sc
1	0.593'11	1.26689	0.46815	45.142
1	1.13724	2.42790	.46838	45.225
1	2.14857	4.58924	.46817	45.149
1	1,10970	2.36945	.46832	45.202
		Average	.46825	45.179
2	1.02956	2.19934	.46811	45.132
2	1.50457	3.21486	.46801	45.094
2	0.90557	1.93409	.46822	45.161
2	1.79432	3.83257	.46817	45.151
2	1.71420	3.66083	.46826	45.174
		Average	.46815	45.142

These results confirm the higher value for scandium found by Hönigschmid, 45.10.

Potassium.—Honigschmid and Goubeau[12] have analyzed potassium chloride. The purified salt was dehydrated successively at 250 and 600° and was finally fused, all in a current of nitrogen. Solution and comparison with silver followed and the silver chloride was quantitatively collected. Samples Ia and Ib were prepared from the most and least volatile fractions of potassium metal which had been subjected to "ideal" distillation by v. Hevesy. Sample IV also was a "heavy" product from an incompleted similar distillation. Samples II, III and V were purified by crystallization as nitrate, chlorate and nitrate, respectively. All were finally crystallized as chloride. Weights are corrected to vacuum. Cl = 35.457.

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[11] Smith, THIS JOURNAL, 49, 1642 (1927).

[12] Hönigschmid and Goubeau, Z. *anorg. allgem. Chem.*, 163, 93 (1927).

TABLE VII

ATOMIC WEIGHT OF POTASSIUM

Sample	Wt. of KCl	Wt. of Ag	Ratio KCl:Ag	At. wt. K	Wt. of AgCl	Ratio KCl:AgCl	At. wt. K
Ia	3.36688	4.87134	0.691161	39.105			
Ia	3.92490	5.67896	.691130	39.102			
Ia	5.14146	7.43908	.691142	39.103			
		Average	.691144	39.103			
Ib	3.50173	5.06648	.691156	39.105			
Ib	3.80806	5.50967	,691159	39.105			
Ib	4.33410	6.27062	.691176	39.107			
		Average	.691164	39.106			
II	4 35574	6.30199	.691169	39.106	8.37351	0.520181	39.104
II	2.39852	3.47045	,691127	39.102	4 61113	.520159	39.101
II	7.15608	10.35431	.691121	39.102	13.75729	.520166	39.102
II					10 89195	.520177	39.104
		Average	,691139	39.103		.520171	39.103
III	4.56305	6.60205	,691157	39.105	8.77205	.520181	39.104
III	4.60793	8.11400	,691142	39.103	10.78097	.520169	39.103
III	4.92368	7.12366	691173	39.107	9 46480	.520210	39.108
III	5.92880	8 57837	,691134	39.103	11 39758	.520181	39.104
		Average	,691152	39.105		.520185	39.105
IV	3.90883	5.65532	.691178	39.107	7 51410	.520199	39.107
IV	4.35246	6 29745	691146	39.104	8 36735	.520172	39.103
IV	5 26221	7.61367	,691153	39.105	10.11599	.520187	39.105
		Average	.691159	39.105		.520186	39.105
V	6 61240	9.56717	,691155	39.105			
V	9.43007	13.64420	.691141	39.104			
V	9 61736	13 91507	.691147	39.104			
		Average	,691148	39.104			
Weighted average of all			,691149	39.104		.520180	39.104

Evidence of isotopic separation is so slight that Honigschmid and Goubeau have not separated Samples Ia, Ib and IV from the others in computing the average. The result is slightly lower than that found in the same way by Richards and Archibald, 39.106, and by Archibald, but higher than that found later by Richards and Stahler, 39.095, and by Richards and Mueller.

The ratio of silver to silver chloride computed from the above weights is 1.328670, a value identical with that found by Richards and Wells.

Argon.—Moles[13] discusses critically earlier work upon the density and compressibility of argon and arrives at the figures 1.7833 and 1.0009, respectively, as the most probable ones. The atomic weight of argon computed from these figures is 39.94.

Baxter and Starkweather[14] have redetermined the density and compressibility of argon which had been purified both chemically and by

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[13] *Moles, Ber., 60, 134* (1927).

[14] Baxter and Starkweather, *Proc. Nat. Acad. Sci.,* 1467 (1928).

fractional adsorption on chilled, dehydrated chabazite until spectroscopically free from all other gases.

TABLE VIII

THE DENSITY OF ARGON

0°. g = 980.616

Sample	Number of adsorptions	Globe IV, 2110.95 ml.	Globe VII. 2117.77 ml.	Average
		P = 760 mm.		
1	3	1,78380	1 78378	1,78379
1	4	1,78366	1,78362	1.78364
1 + 2	4	1,78363	1.78364	1,78364
1 + 2	5	1,78361	1.78356	1.78359
1 + 2	6	1,78378	1,78368	1.78373
1 + 2	7	1.78356	1,78358	1,78357
1 + 2	8	1,78353	1.78361	1.78357
1 + 2	9	1.78355	.....	1.78355
	Average	1,78364	1,78364	1,78364
		P = 506.667 mm.		
1	4	1,18866	1 18869	1 18868
1 + 2	5	1,18877	1 18882	1.18880
1 + 2	6	1.18878	1.18875	1 18877
1 + 2	10	1.18868	.....	1.18868
	Average	1.18872	1.18875	1,18874
		P = 253.333 mm.		
1 + 2	4	0.59420	0.59418	0.59419
1 + 2	7	.59420	.59413	.59417
1 + 2	9	.59422	.....	.59422
1 + 2	10	.59423	.....	.59423
	Average	,59421	,59416	,59419

The deviation from Boyle's Law is calculated in the conventional way from the densities at differentpressures to be 1.00080, and the atomic weight 39.943.

The densities of oxygen, nitrogen, neon and argon at different pressures as found by Baxter and Starkweather are then weighted according to their probable errors and combined in least squares solutions of the best straight line equations for the deviations from Boyle's Law. From these equations are calculated the following values, the limiting value of a molal volume being 22.4146 liters.

TABLE IX

CALCULATED VALUES

	Normal density, obs.	Normal density, calcd.	$\frac{(PV)_0}{(PV)_1}$	Atomic weight
Oxygen	1 42896 (5)	1.428965	1.00093	16 000
Nitrogen	1 25036	1 25037	1.00040	14 008
Neon	0.89990	0 89990	0 99941	20.183
Argon	1 78364	1 78304	1.00089	89 944

Yttrium.—Hönigschmid and H. Frh. Auer von Welsbach[15] have continued the work of Honigschmid and Meuwsen on yttrium (see Report for 1924) using the purest of the three specimens of material previously employed. This sample, which had been purified by Prandtl, originally gave the value 88.95. Further purification from a trace of erbium was effected by Prandtl by removing a ferrocyanide fraction. Conversion to chloride through the oxalate and oxide and gradual dehydration of the chloride in a current of nitrogen and hydrogen chloride was followed by comparing the chloride with silver and weighing the silver chloride. Weights are in vacuum. Cl = 33.457.

TABLE X

ATOMIC WEIGHT OF YTTRIUM

Wt. of YCl_3	Wt. of Ag	Ratio YCl_3 3Ag	At wt of Y	Wt of AgCl	Ratio YCl_3 3Ag	At. wt. of Y
2 24375				4 94021	0 454181	88.931
2 15306	3 56803	0 603431	88 924	4 74088	,454148	88.918
2 18124	3 61466	603443	88 927	4 80278	454162	88.925
2 43852	4 04100	603445	88 928	5 36920	454168	88 926
2 61345	4 33091	,603441	88 927	5 75442	454164	88 924
2 88846	4 78663	603443	88 927	6 35993	454165	88.925
2 60421	4.31565	603434	88 924	5 73423	454162	88.919
2.32309	3 84963	603458	88 931	5 11498	,454173	88 928
2 38370	3 95020	603438	88 926	5 24859	454160	88 923
2 60220	4.31226	603442	88 927	5.72964	,454165	88 925
2 82846	4 68724	.603438	88 926		. . .	. .
	Average	,603441	88 927		454164	88 924

Silver.—Hönigschmid, Zintl and Thilo[16] carefully purified silver nitrate and prepared it for weighing by fusion in a current of pure, dry air. Then the salt was reduced to metal in a current of hydrogen, eventually at 800°. The silver nitrate and silver in most of the experiments were weighed in air and corrected to vacuum in the usual way. In a few experiments, after being weighed in air, both substances were weighed in an exhausted

TABLE XI

ATOMIC WEIGHT OF SILVER

Wt of AgNO	Wt of Ag	Ratio $AgNO_3$ Ag	At. wt. of Ag
10 33791	6 36464	1 57479	107 880
12 33106	7 83023	1 57480	107 877
10 07649	6 39864	1 57470	107 880
10 73593	6 81733	1 57480	107 877
12 97718	8 24067	1,57477	107.883
11 98142	7 60828	1,57479	107.880
11 32714	7 19276	1 57480	107.878
9 71370	A 16829	1 57478	107.881
12 46620	7 91609	1 57479	107 879

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[15] Honigschmid and von Welsbach, Z. *anorg allgem.* ***Chem.*****, 165,** 284 (1927).

[16] Hönigschmid, Zintl and Thilo, ***ibid.***, 163, 65 (1927).

TABLE XI (*Concluded*)

Wt. of $AgNO_3$	Wt. of Ag	Ratio $AgNO_3:Ag$	At. wt. of Ag
11.95961	7.59441	1.57479	107.879
11.38824	7.23156	1.57480	107.878
17.18614	10.91325	1.57480	107.878
12.48205	7.92620	1.57478	107.881
13,96264	8.86633	1.57479	107.879
	Average	1,57479	107.879
	Weighings in exhausted vessel		
11.38833	7.23158	1.57481	107.877
17.18609	10.91327	1.57479	107.880
12.48212	7.92624	1.57478	107.880
13.96267	8.86635	1.57479	107.879
	Average	1.57479	107.879

weighing bottle. The latter procedure raised very slightly the weights of both substances but in the same proportion. N = 14.008.

The average ratio of silver nitrate to silver is identical with that previously found by Richards and Forbes.

Zintl and Goubeau[17] have converted potassium nitrate into potassium chloride by heating in a current of hydrogen chloride. The nitrate, after purification by crystallization, was cautiously fused in bulk and powdered preparatory to weighing. Weighings were first made in air of known density and corrected to vacuum, and then were repeated in an exhausted container. The latter were always smaller with potassium nitrate but usually larger with potassium chloride.

TABLE XII

THE ATOMIC WEIGHT OF SILVER

Air weight corrected to vacuum

Weight of KNO_3	Weight of KCl	Ratio $KNO_3:KCl$
6.88504	5.07669	1.35620
6.88501	5.07663	1.35622
7.70387	5.68084	1.35614
7.70382	5.68075	1.35613
8.14246	6.00415	1.35611
8.14263	6.00404	1.35606
7.81347	5.76152	1.35615
7.81352	5.76144	1.35618
12.78860	9.42974	1.35617
12.78874	9.42995	1.35621
13.04268	9.61686	1.35623
13.04260	9.61716	1.35618
	Average	1.35617

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[17] Zintl and Goubeau, Z. *anorg. allgem. Chem.,* 163,302 (1927).

TABLE XII (*Concluded*)

Weights determined in exhausted container

Weight of KNO_3	Weight of KCl	Ratio $KNO_3:KCl$
6.88476	5.07678	1.356127
7.70331	5,68051	1.356099
8.14250	6.00438	1.356093
8.96711	6 61239	1.356109
7.81340	5 76163	1,356109
12 78839	9 43007	1 356129
13.04224	9 61737	1 356113
	Average	1 356111

With the ratios $KCl/Ag = 0.691149$ and $AgCl/Ag = 1.328668$, the following atomic weights are obtained:

$N = 14.008$

$KNO_3:KCl$	Ag	K	Cl
1.35617	107.872	39.102	35.454
1.356111	107.879	39.104	35.456

Brauner[18] suggests that in Baker and Riley's analyses of silver oxide (see Report for 1926) by reduction, silver might have been lost by volatilization. Baker and Riley[19] reply that owing to abundant opportunity for condensation loss of silver was unlikely, especially in view of the fact that ultimately the weight of the containing tube and silver remained constant on repeated fusion. Brauner[20] contends that a loss of silver by volatilization and condensation as smoke might readily have escaped visual detection, while the relatively small surface offered by fused silver might reduce the rate of volatilization after fusion. Baker and Riley[21] describe experiments to prove that silver, heated as in their experiments for reducing silver oxide in hydrogen, does not escape from the containing tube.

Antimony.—Krishnaswami[22] synthesized antimony tribromide from carefully purified metal which had been extracted from minerals occurring in India and Burma. The tribromide was purified by sublimation in a vacuum and collected in glass bulbs. The various fractions of tribromide, after being weighed, were dissolved in tartaric acid solution and the glass was collected and weighed. Precipitation and quantitative determination of the silver bromide was in two cases preceded by comparison with silver. Vacuum weights are given. Br = 79.920.

Dysprosium.—Hönigschmid and H. Frh. Auer von Welsbach[23] used as a starting point dysprosium sulfate which had been purified by C. Auer von Welsbach. This material was found by x-ray analysis to contain only 0.1% of holmium and a trace of terbium as impurities.

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[18] Brauncr, *Nature*, 119,348 (1927).

[19] Baker and Riley, *ibid.*, 119,349 (1927).

[20] Brauner, *ibid.*, 119,526 (1927).

[21] Baker and Riley, *ibid.*, 119, 703 (1927).

[22] Krishnaswami, *J. Chem. Soc.*, 1927,2534.

[23] Hönigschmid and von Welsbach, *Z. anorg. allgem. Chem.*, 165, 289 (1927).

TABLE XIII

ATOMIC WEIGHT OF ANTIMONY

Source	Wt. of $SbBr_3$	Wt. of AgBr	Ratio, $SbBr_3:3AgBr$	At. wt. of Sb
Commercial Sb_2O_3	4.44079	6.92064	0.641664	121 753
	3.15437	4.91639	(.641603)	(121.719)
	3.64246	5.67747	(.641566)	(121.701)
	3.97152	6.18954	.641650	121.746
	3.47255	5.41185	.641654	121.750
	3.80868	5.93549	.641679	121 762
	3.44766[a]	5 37296	.641669	121.756
	4.12164[a]	6.42335	.641665	121.754
		Average	,641664	121.754
Mysore Stibnite	4 29146	6.6 901	(.641569)	(121.700)
	4 03746	6.2 236	.641645	121.743
	3.85444	6.00720	.641637	121.738
	4.25750	6.63517	.641656	121.749
	4.16876	6.49684	,641659	121.751
	3.40170	5.30160	641636	121 738
		Average	.641647	121,744
Mysore Cervantite	3.35625	5.23081	.641631	121.735
	3.98107	6.20437	,641659	121.751
	3.82381	5.95934	.641650	121.746
		Average	.641647	121.744
Amherst Stibnite	4 61169	7.18715	,641657	121.750
	4 61851	7.19785	.641651	121.746
	4 11282	6.40990	,641635	121.737
	3.50233	5.45818	641666	121.755
	3.98801	6 21524	.641650	121.745
		Average	,641652	121.747
S. Shan States Stibnite	3.74847	5.84185	.641658	121.750
	4.94145	7.70114	,641652	121.747
	3 82442	5.96012	.641668	121.756
		Average	.641659	121.751

[a] In these two analyses comparison with silver gave the values 121.751 and 121.735.

Krishnaswami believes the differences between samples of different origin to be within the experimental error. This outcome contradicts Muzaffar's previous findings.

TABLE XIV

ATOMIC WEIGHT OF DYSPROSIUM

Wt. of $DyCl_3$	Wt. of Ag	Ratio, $DyCl_3:3Ag$	At. wt. of Dy	Wt. of AgCl	Ratio, $DyCl_3:3AgCl$	At. wt. of Dy
2.49132	2.99933	0.830625	162.453	3.98506	0.625165	162.457
2.77037	3.33519	.830648	162.460	.....	.....	.....
2.42773	2.92275	.830632	162.455	3.88325	,625180	162.463
2.76304	3 32629	,830667	162.466	4,41978[a]	,625153	162.452
2.75327	3.31454	,830664	162.465	4.40393	.625185	162.465
295998	3.56349	,830641	162.458	4.73475	.625161	162.455
3.23623	3.89607	.830640	162.457	5.17653	.625174	162.460
	Average	.830645	162.459		.625170	162.459

[a] The weight of dysprosium chloride used in this analysis is apparently given incorrectly as 2.46304.

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ATOMIC WEIGHTS
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	Symbol	At. number	At. weight
Aluminum	Al	13	26 97
Antimony	Sb	51	121 77
Argon	A	18	39.94
Arsenic	As	33	74 96
Barium	Ba	56	137 37
Beryllium	Be	4	9.02
Bismuth	Bi	83	209 00
Boron	B	5	10 82
Bromine	Br	35	79 916
Cadmium	Cd	48	112 41
Calcium	Ca	20	40 07
Carbon	C	6	12 000
Cerium	Ce	58	140 25
Cesium	Cs	55	132 81
Chlorine	Cl	17	35 457
Chromium	Cr	24	52 01
Cobalt	Co	27	58 94
Columbium	Cb	41	93.1
Copper	Cu	29	63 57
Dysprosium	Dy	66	162 46
Erbium	Er	68	167 7
Europium	Eu	63	152.0
Fluorine	F	9	19 00
Gadolinium	Gd	64	157 26
Gallium	Ga	31	69 72
Germanium	Ge	32	72 60
Gold	Au	79	197 2
Hafnium	Hf	72	178 6
Helium	He	2	4 002
Holmium	Ho	67	163 5
Hydrogen	H	1	1 008
Indium	In	49	114 8
Iodine	I	53	126 932
Iridium	Ir	77	193 1
Iron	Fe	26	55 84
Krypton	Kr	36	82 9
Lanthanum	La	57	138 90
Lead	Pb	82	207 22
Lithium	Li	3	6 940
Lutecium	Lu	71	175 0
Magnesium	Mg	12	24.32
Manganese	Mn	25	54 93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	96.0
Neodymium	Nd	60	144.27
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Nitrogen	N	7	14.008
Osmium	Os	76	190.8
Oxygen	O	8	16.000
Palladium	Pd	46	106.7
Phosphorus	P	15	31.027
Platinum	Pt	78	195.23
Potassium	K	19	39 096
Praseodymium	Pr	59	140.92
Radium	Ra	88	225.95
Radon	Rn	86	222
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.44
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	45.10
Selenium	Se	34	79.2
Silicon	Si	14	28.06
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.064
Tantalum	Ta	73	181.5
Tellurium	Te	52	127.5
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.15
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	184.0
Uranium	U	92	238.17
Vanadium	V	23	50.96
Xenon	Xe	54	130.2
Ytterbium	Yb	70	173.6
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

Conversion to chloride through the oxalate and oxide was followed by gradual dehydration in a stream of nitrogen and hydrogen chloride. The weighed, anhydrous chloride was compared with silver in the usual way, and the resulting silver chloride was collected and determined. Weights are in vacuum. Cl = 35.457.

The correction for holmium impurity is only —0.003 unit. The corrected value, 162.456, is somewhat lower than that found by Kremers, Hopkins and Engle, 162.52.

Moles[24] discusses gas density methods and results obtained in recent years. The best values for atomic weights determined in this way are found to be as follows: H = 1.0078; N = 14.008; F = 19.00; Cl = 35.458; Br = 79.918; Ag = 107.880; I = 126.92.

Zintl and Goubeau[25] find the weights of finely divided potassium nitrate and potassium chloride determined by weighing in air and correcting for the buoyant effect of the air in the usual way to be inconstant. Upon fusion the weight of potassium nitrate became constant but the weight was always less than that of the powdered material. Fused, powdered potassium nitrate when weighed in air and corrected to vacuum showed almost invariably a loss in weight (0.00–0.07 mg. per gram) when weighed in an exhausted container, and the weights determined by the latter method were more constant than those determined by the former. On the other hand potassium chloride sometimes weighed less but usually weighed more in a vacuum (0.00–0.05 mg. per gram). The conclusion by the authors is that the results may be explained by variable air adsorption on the surface of the finely divided material.

With the use of an improved mass spectrograph of greater resolving power and accuracy than earlier instruments Aston[26] has determined the deviations from integral values of the masses of the atoms of the following simple or complex elements.

H	1.00778	Cl^{37}	36.980
He	4.00216	A^{36}	35.976
Li^6	6.012	A^{40}	39.971
Li^7	7.012	As	74.934
B^{10}	10.0135	Br^{79}	78.929
B^{11}	11.0110	Br^{81}	80.926
C	12.0036	Kr^{78}	77.926
N	14.008	Kr^{80}	79.926
F	19.0000	Kr^{81}	80.926
Ne^{20}	20.0004	Kr^{82}	81.927
Ne^{22}	22.0048 (?)	Kr^{83}	82.927
P	30.9825	Kr^{84}	83.928
Cl^{35}	34.983	Kr^{86}	85.929

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[24] Moles, *Gazz. chim. ital.*, 56, 915 (1926).

[25] Zintl and Goubeau, *Z. anorg. allgem. Chem.*, 163, 105 (1927).

[26] Aston, Proc. Roy. *Soc. (London)*, **115A**, 487 (1927).

I	126.932	**The other isotopes of tin, xenon and mercury show the same differences from integral values**
Sn^{120}	119.912	
Xe^{134}	133.929	
Hg^{200}	200.016	

The resolution of the lines of tin, xenon, mercury and lead points to the following composition of these elements (see also Aston, *Nature* 120, 224 (1927)).

	Atomic number	Atomic weight	Mass numbers of isotopes in order of intensity
Sn	50	**118.70**	**120,118,116,124, 119,117,122,121, 112, 114,** 115
Xe	54	**130.2**	**129, 132, 131, 134, 136,128,** 130, **126, 124**
Hg	80	**200.61**	**202,200, 199, 198, 201,204, 196**
Pb	82	**207.22**	208, 207, 206, 209 (?), **203** (?), **204** (?)

Aston[27] was unable to distinguish between the mass spectra of ordinary mercury and that found in coal tar.

In the table of atomic weights on page 615, for which the author of this report solely is responsible, changes from the 1927 table are made in the cases of helium,[28] argon, dysprosium, neon and yttrium. The atomic weight of potassium seems to be in some doubt, but further evidence should be awaited before a change.

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THEORIES OF UNIMOLECULAR GAS REACTIONS AT LOW PRESSURES. II

BY OSCAR KNEFLER RICE AND HERMAN C. RAMSPERGER

RECEIVED MAY 16, 1927 PUBLISHED MARCH 7, 1928

Certain gas reactions, termed by Hinshelwood quasi-unimolecular, are unimolecular at high pressures but fall off in rate below the unimolecular law at low pressures. In a recent paper[1] we have attempted, on the basis of collision hypotheses and classical statistical mechanics, to develop equations giving the relation between pressure and rate of reaction. We considered chiefly two theories which led to equations (5) and (19), respectively.

In the former article[1] we applied the theories to the decomposition of propionic aldehyde, which had been studied by Hinshelwood and Thomp-

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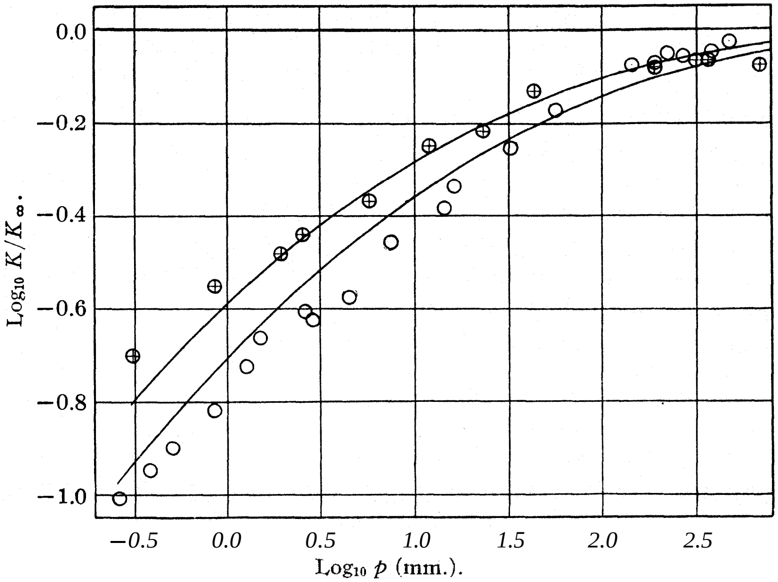
[27] Aston, Nature, 119,489 (1927).

[28] A recent unpublished determination of the compressibility of helium below one atmosphere by Mr. R. B. Ellestad and the author has yielded the value for $(PV)_0/(PV)_1$ of 0.9995. This value combined with the density found by Baxter and Starkweather, 0.17846, gives as the atomic weight of helium 4 002, a result identical with that found by Aston with the mass spectrograph.

[1] Rice and Ramsperger, THIS JOURNAL, 49, 1617 (1927).

son,[2] and found that we could not distinguish between the two theories. In this paper we shall apply our considerations to the decomposition of azomethane.[3]

In this case Theory I does not fit the data at all. If we make the curve fit the upper points it misses the lower ones by a factor of 10. The comparison of Theory II with the data is given in Fig. 1. In making the calculations we set[4] $n = 25$, which makes the rate fall off at about the right pressure, and $\epsilon_0 = 50{,}600$. s is given throughout the value of[5] 6×10^{-8}.



Upper curve, ⊕, 290°C ; lower curve, ○, 330°C.

Fig. I.

It must be remembered that ϵ_0, as given, is not the heat of activation as calculated from the original Arrhenius equation, but is related to it, as shown in our former article by equation (20) for Theory II. We have used the temperature coefficient originally found by Ramsperger.[6] We would now make a second approximation by using the temperature coefficient taken from the K_∞ values from the curves at the two temperatures, but the correction is negligible It may be well to remark that, although the values of many of the quantities involved are known to order of magnitude only, the temperature coefficients of all of them are known, and the relative positions of the curves at different temperatures, as well as their shapes, are fixed, in the plot used, once n is determined.

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[2] Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*,**113A**, *221 (1926).*

[3] Ramsperger, THIS JOURNAL, 49, *1495 (1927).*

[4] For the nomenclature and for the method of fitting curves to data see Rice and Ramsperger, ref. *1.*

[5] Though strictly the theory holds only for initial rate constants, average rates during a run were taken for azotnethane as they were practically the same.

[6] Ramsperger, THIS JOURNAL, 49, 912 *(1927).*

It is now necessary to use equation (24) of our previous article in order to test our assumption that deactivation, or at least sufficient loss of energy, occurs at every collision of an activated molecule. The curves used in the graphical integration of equation (19) for azomethane (which are similar to those of Fig. 1 of our previous paper) show that at the lowest pressure used at 330° approximately only 11.5% of the reaction was due to molecules having a greater energy than 62,600 calories per mole. The energy of an average molecule at this temperature, from our value of n, is about 15,000. Let us then take $\epsilon' = 77{,}600$ in equation (24); and let us take $\epsilon'' = 57{,}600$, since molecules of this energy lack equilibrium numbers by only 5%. (The number of molecules actually present is to the number present at equilibrium as the integrand in equation (19) is to the integrand at infinite pressure.) The value of (24) evaluated by a more accurate method than formerly used is less than 0.013, which is so small that Theory II needs no modification.

Correction to Previous **Article.**—The sentence below Fig. 1 should read: "At $\epsilon - \epsilon_0$ equal to 5000 the concentration lacks about 8% of the equilibrium value."

Note on Diethyl Ether

Hinshelwood has recently studied the decomposition of diethyl ether.[7] This fits Theory II a little better than Theory I. On Theory II it requires a value of n of 6.

Discussion

One of the most striking features of the results is the difference in the number of degrees of freedom[8] in the various cases. The number of degrees of freedom of azomethane fits well with the specific heats of similar compounds, C_p for acetone being about 24 calories per mole per degree in the range from 129 to 233°.[9] But the numbers of degrees of freedom of the propionic aldehyde and diethyl ether are surprisingly low; the specific heat of ether is about 44.5 calories per mole per degree at 350°. This might be due to some impedance to the transfer of energy in the molecule, only a few degrees of freedom being in communication in the proper place in the molecule, so the molecule acts like one with a smaller number of degrees of freedom.

One objection that might be brought against our interpretation of the results is the possible presence of some sort of a chain reaction, as the decomposition of azomethane is undoubtedly exothermic.[10] If this is

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[7] Hinshelwood, Proc. Roy. *Soc.* (London), **114A,** 84 (1927).

[8] By the number of degrees of freedom we mean, as explained in our previous paper, the number of quadratic terms in the energy expression. C_v in calories is then approximately equal to the number of degrees of freedom.

[9] Landolt-Börnstein, "Tabellen," 1923, p. 1275.

[10] Azomethane explodes, presumably of course, with evolution of heat, when an electric discharge passes through it. The products are different from the products of thermal decomposition and contain a little over 20,000 calories more energy per mole of azomethane decomposed (estimated by us from heats of combustion). The heat of reaction must, therefore, be more than 20,000 calories per mole of azomethane [see Thiele, Ber., 42, 2575 (1909)].

the chief means of activation at low pressure, and unless the mechanism of transfer of energy is very specific, we would expect the reaction rate to fall off during the course of a run as the products of reaction accumulate but practically this is not the case, though the run falls off in most cases to a very small extent. What the effects of simple local-heating might be, and whether such an effect could be combined with our theory to give satisfactory results, we cannot at present decide.

Summary

Two theories based on collision hypotheses of quasi-unimolecular reactions, which we have previously developed, are applied to the decomposition of azomethane. It is possible to explain the falling off of the rate with pressure and to decide between the two theories. The efficiency of activation and deactivation at collision is considered, and the following are discussed: (1) the number of degrees of freedom involved in the various cases; (2) the effect of heat of reaction in the case of azomethane. The decomposition of diethyl ether is also considered briefly.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

AN ATTEMPT TO PREPARE TRIATOMIC HYDROGEN[1]

BY HUGH M. SMALLWOOD[2] AND H. C. UREY

RECEIVED JUNE 9, 1927 PUBLISHED MARCH 7, 1928

Introduction

The preparation and properties of an active modification of hydrogen, supposed to be triatomic, have been described by a number of investigators[3]. According to their papers, whenever hydrogen is ionized or dissociated a small amount of active product is formed. The activating agents that have been used with success include a-particles, the Siemens ozonizer, the vacuum discharge and the corona discharge. It has also been stated that if oxygen is burned in an atmosphere of hydrogen, or if hydrogen-oxygen mixtures containing deficiency of oxygen are detonated, part of the hydrogen remaining after the combustion is activated. It has furthermore been reported that hydrogen is activated by passage over

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[1] Extract from Dissertation submitted by Hugh M. Smallwood in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Du Pont Fellow in Chemistry.

[3] (a) Duane and Wendt, *Phys. Rev.*, [2] 10,116 (1927); (b) Wendt and Landauer, THIS JOURNAL, 42, 930 (1920); *(c)* 44, 510 (1922); (d) Newman, *Phil. Mag.*, 43, *455* (1922); (e) Venkataramaiah, *Nature*, 106, 46 (1920); (f) 112, 57 (1923); (g) *Chem. News*, 124, 323 (1922); (h) THIS JOURNAL, 45, 261 (1923); (i) Venkataramaiah and Swamy, *Proc. Sci. Ass. Mah. Coll. Viz.*, p. 23, Dec., 1922; (j) Grubb, *Nature*, 111,600, *671* (1922); (k) Paneth, *Z. Elektrochem.*, 30, 504 (1924); (l) Anderegg, THIS JOURNAL, 47, 2429, (1926).

heated metals such as platinum and palladium. Of these various methods of preparation the passage of hydrogen over heated metals or through the ozonizer is said to be the most readily performed.

This modification of hydrogen has been reported to have the property of reducing sulfur, arsenic, phosphorus, nitrogen, etc., at room temperature to form the corresponding hydrides, and it is this characteristic that has been used to test for the material. It is not completely destroyed upon passage through glass wool, as is monatomic hydrogen, and it is described as having a period of half-life of the order of several minutes. It retains its activity upon condensation at liquid air temperatures and subsequent evaporation. Wendt and Landauer[3b,c] state that it is catalytically decomposed by platinum, nickel, copper, lead, antimony and cadmium, but that it is not affected by silver, molybdenum, mercury, tin, bismuth, zinc or aluminum. They further observed that its preparation in a closed system is accompanied by a decrease in pressure. It is this observation that has led to the assumption of a triatomic molecule.

Recent workers, however, have been unable to duplicate these results. Bach,[4] Scanavy-Grigoriewa[5] and Paneth, Klever and Peters[6] were unable to obtain evidence of activation upon passing hydrogen over heated metals. The latter authors also report unsuccessful attempts with the ozonizer, bombardment with a-particles and detonation of hydrogen-oxygen mixtures. Curtius,[7] moreover, was unable to obtain activation with the ozonizer. On the other hand Elliott,[8] working with a similar apparatus, reports a large number of positive results including quantitative studies of the effects of the conditions of the various experiments upon the extent of activation.

There are therefore many contradictions in the past work on active hydrogen. The present paper describes a series of experiments attempting the preparation of this active hydrogen. The methods of the former workers have been repeated and, in some cases, extended. Throughout the work the results have been negative.

Experimental

1. Corona Discharge and Ozonizer.—The apparatus used in these experiments and those to be described was built of Pyrex glass throughout. The corona tube was similar to that employed by Wendt and Landauer in the previous work on this method. It consisted of a Liebig condenser about 1 m. long. The high tension electrode was a bare aluminum wire, 0.6 mm. in diameter, strung along the axis of the central tube of the condenser by means of tungsten hooks, the latter being sealed through the glass at each end of the central tube. A salt solution circulated through the cooling jacket

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[4] Bach, *Ber.*, 58B, 1388 (1925).

[5] Scanavy-Grigoriewa, *Z. anorg. allgem. Chem.*, 159, 55 (1926).

[6] Paneth, Klever and Peters, *Z. Elektrochem.*, 33, 102 (1927).

[7] Curtius, *Diss.*, Heidelberg, 1926.

[8] Elliott, *Trans. Faraday Soc.*, 23, 60 (1927).

served as the ground electrode. The central tube, through which the hydrogen passed, was 1.2 cm. in diameter. The tube was operated at a potential of 11–12 kv. with 60 cycle alternating current. This gave a fairly uniform discharge from the central wire

The method used to determine the extent of activation was first developed by Wendt and Landauer.[3b,c] It is carried out as follows. After leaving the discharge the hydrogen is passed over glass wool (to remove atomic hydrogen) and is then mixed with nitrogen, the resulting mixture being scrubbed with 100 cc. of water. The presence of an active form of hydrogen results in the formation of ammonia, which is absorbed in the scrubbing water and determined by the usual Nessler test. The delicacy of this test was shown in the blank runs. These showed the absence of ammonia in the hydrogen and nitrogen used, but upon passing the hydrogen through the discharge without subsequent mixing with nitrogen, ammonia was found to be present to the extent of 0.0001% of the hydrogen passed. Presumably this was caused by the impurity of the original hydrogen. Both the hydrogen and the nitrogen were taken from cylinders, the nitrogen being bubbled through alkaline potassium pyrogallate and concentrated sulfuric acid.

Two thirty minute runs with this apparatus in which the pressure was maintained at one atmosphere and the temperature at room temperature, the rates of flow being 1400 and 180 cc. (0° and 760 mm.) of hydrogen per minute, respectively, failed to show an appreciable activation of the hydrogen in that the test for ammonia was no larger than that appearing in the blank run. The linear velocities of the gas flowing varied from 160 cm. to 1200 cm. per minute and the time spent in the ozonizer from 0.6 to 0.08 minute. This appears to be a sufficiently high velocity to insure removal from the activating zone and a sufficient time in the ozonizer to secure activation. Wendt and Landauer report only the volumes of hydrogen flowing per minute and not the dimensions of the apparatus, but from their description of their apparatus we believe that we have used both a wider range of linear velocities and times of activation than did these authors.

It was thought that this failure might be due to aluminum sputtered off the central electrode onto the glass walls. To remove this difficulty a Pyrex tube 4 mm. in diameter was inserted in place of the central electrode, being supported by a ring seal at each end. This tube was filled with salt solution and connected to the high tension terminal of a large spark coil. A uniform brush discharge throughout the tube was obtained with this set-up. Before commencing the actual runs the inside of the discharge tube was washed out with dilute hydrochloric acid and distilled water. Several half hour runs at atmospheric pressure and rates of flow of 400 to 800 cc. of hydrogen per minute gave no indication of the presence of an active form of hydrogen.

2. Combustion of Oxygen in Hydrogen.—The apparatus used was essentially the same as that employed by Venkataramaiah in the original work on this method. A large bulb was filled with hydrogen and the rate of flow of hydrogen through the bulb adjusted to a convenient value. Oxygen was then admitted through a platinum jet (8 mm. in diameter) and ignited by means of sparking points sealed through the wall of the bulb near the jet. The oxygen stream was regulated to give a flame about 3 cm. long. The products of combustion were passed through glass wool, over flowers of sulfur and finally directed against a piece of filter paper dipping into lead acetate solution. No formation of hydrogen sulfide could be detected with this apparatus.

3. Passage of Hydrogen over Hot Wires.—Hydrogen was passed over an electrically heated coil of nickel wire hung loosely from a horizontal porcelain tube. The temperature of the wire was varied from a dull red to the melting point of nickel. The rate of flow of hydrogen was varied through wide limits and in some experiments the gas was saturated with water by bubbling through water prior to entering the apparatus.

The hydrogen leaving the apparatus was led over flowers of sulfur and tested with lead acetate. No indications of the presence of an active modification of hydrogen were obtained although each new piece of nickel wire produced a very minute amount of hydrogen sulfide. In the light of the work of Bach and others (*loc. cit.*) these faint tests were interpreted as being due to some form of sulfur present in the original wire but which was soon exhausted.

Further experiments with platinum wires and the tungsten filament from a Mazda lamp gave no tests for hydrogen sulfide, although in some cases the wire was hot enough and the flow of hydrogen sufficiently great to melt the sulfur and even distil it into the lead acetate solution.

4. **Vacuum** Discharge.—The major part of the time spent on this research was devoted to an effort to determine whether or not an active modification of hydrogen capable of passing through a plug of glass wool is present in the gases drawn from a vacuum discharge.

Throughout this part of the work electrolytic hydrogen was used, the electrolyte being a 30% solution of potassium hydroxide. The hydrogen was passed through asbestos to remove as much as possible of the alkaline spray, and then passed over heated platinized asbestos to remove any trace of oxygen. In some experiments the hydrogen was dried with liquid air.

The first apparatus set up was, as nearly as possible, an exact replica of that used by Wendt and Landauer. This consisted of a discharge tube 10 cm. long from which the hydrogen was led over glass wool, then over flowers of sulfur and finally over a strip of filter paper dipping in lead acetate solution. No hydrogen sulfide was formed in this apparatus upon running it for as long as half an hour, although Wendt and Landauer report large tests at the end of three minutes. The pressure in the discharge was varied from 2 to 7 cm. of mercury and the rate of flow of hydrogen was varied through a wide range.

This method of detecting a small amount of hydrogen sulfide does not seem particularly delicate. To remedy this defect and to permit working at lower pressures another procedure was developed. The lead acetate bubbler was replaced with a trap filled with silica gel, which was activated by heating at 300–350° for one hour in a current of hydrogen at a pressure of 1–2 mm. The apparatus was then filled with hydrogen at atmospheric pressure and the gel heated for another fifteen minutes in a slow current of hydrogen which was led out of the apparatus and bubbled through a solution of lead acetate acidified with acetic acid. This was done to show that all of the sulfur had been removed from the gel. If this blank was satisfactory a run was made during which the gel was cooled with liquid air. At the conclusion of the run the apparatus was again filled with hydrogen and the heated gel swept out into the lead acetate solution as before. Although much more laborious than the methods used by previous workers, this procedure enabled the detection of exceedingly minute amounts of hydrogen sulfide.

On using this more delicate test it was found to be extremely difficult to obtain good blank tests. Commercial flowers of sulfur were found to contain fairly large amounts of volatile sulfides. To remedy this a very pure form of sulfur was prepared by acidifying a solution of sodium thiosulfate with hydrochloric acid and filtering off and distilling the precipitated sulfur. It was next found that in the course of a thirty-minute run enough sulfur could distil over into the gel to give fairly large amounts of lead sulfide, the elementary sulfur, of course, being reduced upon passing through the heated gel in the presence of hydrogen. This effect was eliminated by adjusting the Dewar flask holding the liquid air, in which the gel was immersed, in such a manner that the liquid air level stood 5–10 cm. above the top of the gel. The sulfur condensed to an opalescent film immediately upon reaching the cold tube. Upon removing the liquid air the hydrogen sulfide evaporated and could be swept out of the gel by heating without disturbing the sulfur condensed some distance away. Employing these precautions it was found possible to obtain perfect blank tests both upon running the discharge with no sulfur in the apparatus and upon passing the hydrogen over the sulfur in the absence of the discharge.

In the course of an actual experiment the hydrogen passed out of the discharge, through a plug of glass wool 10 cm. long and finally over the sulfur. At this point any of the active form present would react to form hydrogen sulfide, which would be adsorbed on the gel and would, at the end of the experiment, be made evident by the precipitation of lead sulfide. Such experiments frequently resulted in the formation of a small amount of precipitate but the tests so obtained were so minute and erratic that they could not be definitely ascribed to the presence of an active modification of hydrogen.

The conditions under which the various experiments were carried out were as follows. The pressure was varied in different runs from 1 to 80 mm. At the lower pressures rates of flow of 20–30 cc. per minute were used and at the higher pressures the rate was maintained at 200 cc. per minute, both volumes being measured under standard conditions. Throughout the low pressure work Wood[9] discharge tubes about 1 m. long were used. These were run with wet hydrogen, giving the red discharge due to atomic hydrogen, and with dry hydrogen, in which case the secondary spectrum was most prominent. The hydrogen to be tested was tapped off either in the middle of the tube or near one of the electrodes, since Smyth and Brasefield[10] have found that at that point in the discharge there are large amounts of H_3^+. The sulfur was inserted 15–30 cm. away from the discharge, connection being made with 7mm. glass tubing. In some of the experiments the discharge tube was cooled with tap water, with salt-ice mixture or with carbon dioxide snow and ether.

The experiments at higher pressures were carried out in smaller discharge tubes of the general type used by Wendt and Landauer. These were water cooled throughout. In some cases a condensed discharge was used, producing the atomic spectrum at a pressure of several centimeters.

During the whole series of experiments sporadic tests were obtained but these were so small that it was necessary to run for thirty minutes or more in order to produce a visible amount of lead sulfide. The size of the tests seemed to have no connection at all with the experimental conditions under which they were obtained. Efforts to show that the substance producing them was unstable enough to decay when led through a by-pass 4 m. long and 2 cm. in diameter before reaching the sulfur were not conclusive because of the strong fatigue effect observed in all the tubes. Attempts to rejuvenate a spent tube by washing with dilute hydrochloric acid, sodium hydroxide and distilled water were only partially successful. The great difficulty encountered in the whole work was that it was not possible to make a series of consistent runs in order to determine, for example, whether or not cooling the discharge had any effect on the size of the precipitate. No tube could be found that, when operated under identical experimental conditions, would give the same amount of lead sulfide three times in succession.

Wendt and Landauer have sought to obtain evidence for their assumption of a triatomic molecule by showing that the activation of hydrogen in a closed system is attended with a decrease in pressure. This experiment has been repeated and part of the original results confirmed. The apparatus used consists of a U-shaped discharge tube equipped with platinum electrodes and attached to a small closed arm manometer. If a discharge is passed at a hydrogen pressure of 9 cm. of mercury and at liquid air temperatures, there is a considerable pressure drop provided the electrodes are immersed

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[9] Wood, *Proc. Roy. Soc. (London)*, *97*, 455 (1920).

[10] Smyth and Brasefield, *Proc. Nat. Acad. Sci.*, *12*, 443 (1926).

in the liquid air. If, however, the electrodes are not immersed in liquid air there is no effect. Wendt and Landauer report that the discharge has a yellow or greenish yellow color. In the repetition the discharge was the usual pale blue color throughout.

Discussion

The experiments just described indicate that, under the experimental conditions detailed, there is no appreciable activation of hydrogen. The failure of duplication of the results of the original workers may be accounted for in a number of ways. In the first 'place none of the papers announcing positive results report adequate blank experiments. All of the investigators were careful to ensure the absence of the particular hydride which was later to form the test from the hydrogen used in the work, but none report experiments designed to show that there was no source of sulfur or nitrogen, as the case might be, sufficiently near to the activating agent to cause the tests. Thus a little elementary sulfur blown back into a discharge can account for many of the results ascribed to H_3. On the other hand, the experiments described by Duane and Wendt and by Wendt and Landauer were so numerous and of such varied nature that it is difficult to account for them by assuming contamination of the apparatus. Although Elliott's results are detailed and self-consistent they are open to criticism on the ground that he did not sufficiently guard against the possibility of sulfur dust being blown back into the discharge. If his results were due to an active hydrogen, they fail to check those of previous workers in a number of instances. Thus he finds a much shorter period of half life than that reported by Duane and Wendt. This fact suggests a correlation between his work and that of Anderson[11] and of Mitchell and Marshall,[12] who found that the temperature at which copper oxide begins to react with hydrogen is decreased if platinum is placed in the hydrogen stream a short distance in front of the copper oxide. They showed that the effect was due to an unstable modification of hydrogen with an extremely short life. It is possible that some of these positive results may have been due to hydrogen molecules in metastable vibrational and rotational state. The question of blank tests, however, certainly deserves more attention than it has received. All of the papers, excepting the two last cited, in which the necessary controls are reported, record uniformly negative results.

An unknown catalytic effect might account for the uncertainty of the results. This could hardly be an anticatalytic effect since cylinder hydrogen has been used successfully. On the other hand, the hydrogen used in the greater part of the previous work could only have contained minute traces of water vapor, nitrogen or argon. The hydrogen used in the present work must have contained all of these gases as impurities

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[11] Anderson, J. *Chem. Soc.*, 121, 1153 (1922).

[12] Mitchell and Marshall, *ibid.*, 123, 2448 (1923).

at one time or another. It seems unlikely that it is a question of the catalytic effect of the walls of the apparatus since, if this were the case, it should have been observed by the first workers in the field.

The pressure drop experiments fail to add any evidence since hydrogen is readily taken up by metallic electrodes and may be driven into the glass walls to an appreciable extent. In this connection it is interesting to note that in 1908 Fischer and Iliovici[13] subjected hydrogen at atmospheric pressure and liquid air temperatures to the silent discharge in a tube with *external* electrodes. They found a decrease in pressure of 0.5 mm. but, since this was less than their experimental error, they concluded that there is no new molecular species formed under these conditions. Wendt and Landauer's work would lead one to expect *a* large pressure drop in such an experiment. Furthermore, the pressure drop observed by them and duplicated by us was so large that, had it been due to the formation of H_3, it is extremely unlikely that the other experiments with the vacuum discharge would have been negative.

The only conclusion that can be drawn, therefore, is that the existence of triatomic hydrogen has not yet been established. Assuming that there is such a substance, however, it is more difficult to prepare than has been formerly supposed.

Summary

1. Unsuccessful attempts to prepare H_3 by means of the corona discharge, ozonizer, combustion of oxygen in hydrogen, passage of hydrogen over hot metals and the vacuum discharge are described.

2. The previous work on this subject is discussed with the conclusion that the existence of H_3 is not as certain as has been supposed.

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[13] Fischer and Iliovici, *Ber.*, **41**, 4452 (1908).

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

THE SPECIFIC HEAT OF HYDROGEN GAS AT LOW TEMPERATURES FROM THE VELOCITY OF SOUND; AND A PRECISION METHOD OF MEASURING THE FREQUENCY OF AN OSCILLATING CIRCUIT

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At room temperature the specific heat of hydrogen gas is but slightly less than the classical value for a diatomic gas without vibrational energy. This theoretical value is 5/2 R for specific heat at constant volume, where R is the gas constant expressed in the same units as the specific heat. It was found by Eucken,[1] who filled a calorimeter with hydrogen gas under pressure, that below room temperature the specific heat of hydrogen becomes less and approaches the value 3/2 R at a temperature a little below the boiling point of liquid air. A number of specific heat equations, based on quantum theory, have been proposed[2] and accordingly it seemed advisable to make, if possible, a more accurate experimental determination of the specific heat of hydrogen over this range of temperature. Since the moment of inertia of the unresonated hydrogen molecule is not known, it is an undertermined constant in the specific heat equations. However, apparently no theories fit our data. (See end of this paper.)

The experimental method chosen for the specific heat measurements was to determine the velocity of sound by Thiesen's[3] method of closed cylindrical resonators. This method was much improved by Grüneisen and Merkel,[4] who used oscillating circuits and a telephone in place of the siren used by Thiesen for the excitation of the sound in the gas. Grüneisen and Merkel worked at 0°, using both air and hydrogen. The most important further apparatus used by us was a means of obtaining the required constant low temperatures in a resonance tube 150 cm. long, and a means of measuring the frequency of an oscillating circuit (of constant frequency) with an accuracy of $^1/_{30,000}$. If the suitable number of comparison circuits (each with suitable frequency) are set up, the method can be used for measuring the frequency of *any* oscillating circuit which can be excited by radio tubes; the mean frequency over a period of fifteen minutes could (if desired) be measured with an accuracy of $^1/_{1,000,000}$, even

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[1] (a) Eucken, *Sitzb. preuss. Akad. Wiss.*, 1912, p. 128; (b) Scheel and Heuse, *ibid.*, 1913, p. 44; (c) *Ann. Physik*, 40, 473 (1913).

[2] (a) Einstein, *Ann. Physik*, [4] 22, 180 (1907); (b) Reiche, *ibid.*, 58, 657 (1919); (c) Tolman, *Phys. Rev.*, [2] 22, 470 (1923); (d) Kemble and Van Vleck, *Phys. Rev.*, [2] 21, 381, 653 (1923); (e) Dieke, *Physika, Nederlandsch Tijdschrift voor Natuurkunde*, 5e, 412 (1925).

[3] Thiesen, *Ann. Physik*, 24, 401 (1907); 25, 506 (1907).

[4] (a) Grüneisen and Merkel, *Z. Physik*, 2, 277 (1920); (b) *Ann. Physik*, [4] 66, 344 (1921).

if the circuit oscillates only once per second. The only limitation of accuracy is due to the clock used to send the time signals, and to the constancy of the oscillating circuit.

Because of the low density of hydrogen gas, one must use resonance tubes of large diameter, to cut down damping. Because of the relatively long wave length of even the highest easily audible pitches (for example, 10,000 cycles per second) in a light gas, a longer resonance tube is required than with a heavier gas. An apparatus sufficient for determining the velocity of sound in hydrogen would give extremely accurate results with a heavier gas. In the latter case, however, the corrections for "imperfections" in the gas become larger, so that good data of state become necessary.

Calibration of Thermocouples.—For calculating specific heats from the velocity of sound, an error of 0.1°K. at 80°K. produces an error of 0.01 R in the specific heat. Accordingly, two separate thermocouples (C, Fig. 1) were used in all work, to detect any electrical defect appearing in the temperature element. For calibration, a hydrogen thermometer bulb was placed in the inner Dewar (D_2, Fig. 1) in place of the resonance tube. The pressure of the hydrogen was read to about 0.03 mm. by a Gaertner standard steel meter scale, using a cathetometer for interpolation. The bulb of the thermometer connected with the manometer by a capillary tube, and the dead space volume of hydrogen in the manometer was less than 3 cc. The hydrogen was made as for the velocity of sound work, taking special precautions to remove water vapor. Before filling, the thermometer bulb was evacuated for a week by a Cummings mercury vapor pump, using a McLeod gage. The gas pressure at the ice point was about 100.0 cm.

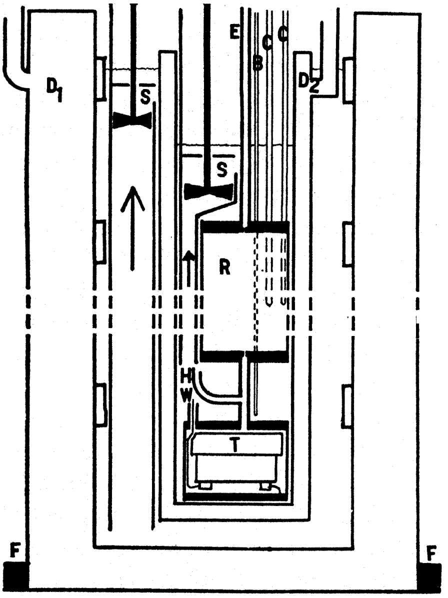

Fig. 1.—Resonator, showing temperature control.

The absolute temperature is not strictly proportional to the height of the mercury column; the necessary corrections are:

FIRST, the imperfections of the thermometer gas (see Equation 18).

SECOND, by combining the volume expansion of mercury with the linear expansion of steel for a 100cm. column at a temperature of 1° above the reference temperature (arbitrarily taken as 20°), a correction of 0.17 mm. in the mercury height (representing about 0.05" in temperature) is needed. The temperature of the mercury column was found by hanging calibrated mercury thermometers along it. The manometer was encased in a wooden box, and read through a plate-glass door.

THIRD, the pressure coefficient of the thermometer bulb was measured by filling with water, changing the pressure, and noting the rising and sinking of the water level in an end tube of known diameter. About two-thirds of the observed compression was accounted for by the known compressibility of water. The calculated correction is of course 0.000" at 273°K., and below that point the Charles' law temperature must be decreased by 0.001" at 250°K., and by 0.002° at 200°K. or any lower temperature down to 50°K.

FOURTH, the dead space and gradient space. To make these corrections small a large bulb (2410 cc.) of hydrogen was used. Volumes were measured by weighing mercury (water for the bulb). The gradient length of capillary was very short, but three thermocouples were firmly mounted on it, and their readings were considered. A thread of black glass was sealed into the top of the dead space of the manometer, and the volume of the dead space measured to the lower tip of the thread. During runs the top of the lower meniscus could be adjusted to *below* the tip of the black glass thread, since the diameter of the manometer tube was accurately known.

FIFTH, .variations in capillary depression of mercury menisci. This affects both the observed pressure and the dead space volume; the latter variation is negligible in our apparatus. The diameters of the manometer columns were 1.65 cm. From a rough extrapolation of a table given by Guyot[5] with the help of some measurements by Palacios,[6] one finds that a change of 0.4 mm. in the height of a meniscus affects the pressure reading by 0.01 mm.

SIXTH, the thermal contraction of the Pyrex thermometer bulb gives a considerable correction, which has been calculated by Dr. R. M. Buffington from the measurements of Buffington and Latimer.[7] We copy Buffington's table as Table I; from a plot the correction at any temperature can be read.

During measurements a vacuum of 0.0001 mm. or better was maintained over the upper meniscus.

In some of the work one thermocouple read as much as 2 microvolts different from the other. This is not serious, since our four-junction

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[5] Guyot, 4th edition of Smithsonian Physical Tables.

[6] Palacios, *Physik. Z.*, 24,154 (1923).

[7] Buffington and Latimer, THIS JOURNAL, 48, 2306 (1926).

TABLE I

CORRECTION TO CONSTANT VOLUME HYDROGEN THERMOMETER DUE TO THERMAL EXPANSION OF PYREX GLASS, ACCORDING TO BUFFINGTON

To be *subtracted* from Charles' Law temperature below the ice-point; added above the ice-point.

Abs. temp., °K.	Correction, °K.	Abs. temp., °K.	Correction, °K.
315.9	+0.159	185.1	−0.150
298.0	+ .088	130.4	− .155
273.1	+ .000	118.2	− .152
248.9	− .053	88.7	− .118
218.3	− .110		

couple gives from 180 to 75 microvolts per degree over the range used in this work. The true e.m.f. was taken as the mean of the readings of the two couples; it was assumed that the temperature was 273.1°K. when this mean reading was zero.

From the equations given by Eastman and Rodebush[8] for the e.m.f. of a certain four-junction copper-constantan thermocouple, the e.m.f. was calculated for the various temperatures at which we used the hydrogen thermometer. These values were larger than our measured values and the ratios were calculated. The results are in Table II, in the order taken. All points represent from 3 to 6 determinations, any one of these series of 3 to 6 determinations being taken at one time, over a period of about half an hour. During this time the temperature of the apparatus drifted from 0.05 to 0.5°, but the results were calculated for the mean temperature by using d (e.m.f.)/d T. In all but two determinations the temperature difference between the top and bottom of the apparatus was 0.02° or less. In the series at 158.61° the difference became 0.05'' and in the one at 134.87° the difference became 0.25°. This temperature difference was noted by differential thermocouple "B" (Pig. 1), and was due to heat leak at the top of the inner Dewar, since the inner bath was warming up although the outer bath was several degrees colder. At 135°K. the viscosity of the petroleum ether becomes large enough so that the stirring propellor cannot effectively equalize the temperature. This effect was avoided in the next measurement at 135°K. by filling the outer Dewar with liquid air. There is very little radiation at these temperatures and the cold air boiling off from the outer bath keeps the top of the inner Dewar cold. Even so, it was necessary to stir for three hours to obtain a uniformity of 0.02° at 133°K.

The lower temperatures for the velocity of sound measurements were calculated from the Eastman and Rodebush equations, applying the factors given in Table II.

For temperatures above 0° the boiling point of water was checked against our thermocouples a number of times. The e.m.f. was 1.01360 times

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[8] Eastman and Rodebush, THIS JOURNAL, 40, 489 (1918).

TABLE II

CALIBRATION OF THERMOCOUPLES

Abs. temp., °K.	E.m.f. (E. and R.)/e.m.f. (obs.)	Abs. temp., °K.	E.m.f. (E. and R.)/e.m.f. (obs.)
284.98	1.0484	134.87	1.04679
273.09	"Ice point"	273.10	"Ice point"
234.04	1.0460	81.27	1.04836
203.36	1.0467	152.53	1.0469
185.97	1.0473	133.17	1.04694
158.61	1.0470	273.13	"Ice point"

that calculated from the table of L. H. Adams.[9] All our temperatures above 0° were calculated from Adams' table, using this same factor. This sort of procedure has been used before in this Laboratory for temperatures not below the boiling point of liquid air.[7]

We have four checks on our scale. The freezing point of mercury was measured as 234.24°K. while the accepted value is 234.22°. The transition point of sodium sulfate was measured as 305.51°, instead of 305.5°K. Finally, we placed together, in a liquid air-bath, the old Laboratory standard of Eastman and Rodebush,[8] our thermocouples and thermocouple "No. 17" of Giauque, Buffington and Schulze.[10] The three temperatures obtained are, respectively, 81.75, 81.77 and 81.92°K. The same comparison a year earlier of ours with the Eastman and Rodebush couple gave a difference of 0.00°.

The Resonator Tubes for the Gas (see Fig. 1).—Four different resonance tubes, 168 cm. or less in length, were used. They were made from brass tubing, the ends being closed with brass plates. The plates were soldered in place, after measuring the thicknesses and drilling central 1mm. holes. These holes were each 1 mm. long, and led into $^{3}/_{16}$-inch thin walled brass tubing. The tubing was fastened with silver solder and served to carry the sound in and out of the various resonators. Larger sized tubing was not used in order to damp out or broaden resonance maxima due to vibrating gas in these end fittings. Smaller tubing ($^{1}/_{8}$-inch diameter) was tried, but did not transmit sound well enough when filled with hydrogen, although it was satisfactory for air.

The lengths of the resonators were determined by comparison with a Gaertner steel meter scale, using a cathetometer as intermediate. Temperature corrections were made, assuming the steel scale to be exactly 1 meter long at 20° as stated by the makers and using expansion coefficients of 0.18×10^{-4} per degree for brass and 0.11×10^{-4} per degree for steel. The end thicknesses were subtracted from the lengths as determined by the cathetometer (Table III).

TABLE III

DIMENSIONS OF RESONATORS AT 0° (NO. 168 AT 20°)

Number	Length inside, cm.	Diam. inside, cm.	Wall thickness, in.	Total end thickness, cm.
150 A	149.969	4.790	$^{1}/_{16}$	1.318
150 B	150 291	2.400	$^{1}/_{32}$	1.323
100 A	99 978	4.785	$^{1}/_{16}$	1.316
168	168.173	9.87	$^{3}/_{64}$	1.295

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[9] "International Critical Tables," 1, 58 (1926).

[10] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

The accuracy of the lengths is 0.01 cm. or better. As the end surfaces of the resonators were not exactly perpendicular to the long axes, determinations 90 degrees apart were made of each length, and the average was taken. As much as 0.04 cm. difference in the length as measured along two opposite sides was found in one resonator (No. 150 A).

Sound in the resonators was heard through the $^3/_{16}$-inch tubing E, 30 cm. or more in length, with the ear pieces from a stethoscope fastened to the free end of the $^3/_{16}$-inch tube by a short piece of rubber tubing. During measurements, hydrogen gas was flowing out through the stethoscope into the ear of the observer. The stethoscope was most sensitive when not clamped tightly in the observer's ear, but held loosely. This effect was later avoided by by-passing the escaping hydrogen so it did not build up a pressure in the observer's ear. The only setting made while listening is a variable condenser, which is adjusted to give a maximum of sound (see below).

A too rapid flow of hydrogen through the apparatus produced uncertainty. The noise of vacuum pumps or talking was troublesome; these distractions were eliminated during all the velocity measurements. Stirring motors were shut off during actual setting of the resonant frequency.

At one time while working at low temperatures, a very baffling difficulty was found to be due to atmospheric air being drawn into the apparatus through tube "W," due to gravitation; this was later prevented by proper precautions.

As the resonators were mounted vertically in a thermostat, the telephone "T" was encased in a copper can, fastened at the bottom of the resonator (Fig. 1). The telephone was activated by an amplifier, the lead wire W (broken off in Fig. 1) being insulated by a small-sized rubber tube, encased in a steel tube. Tests showed a large fraction of the energy from the amplifier to be lost, due to the capacity between the lead wire and the encasing tube, for the return from telephone to amplifier was made by grounding to the apparatus. This loss was worst with frequencies of 10,000 per second or higher. The hydrogen was led into the short tube connecting the telephone and resonator by means of a copper tube H running from top to bottom of the thermostat. A very slow stream of the gas flowed around the telephone, and out through the steel current conduit so that gas in the telephone could not flow through the resonator. The main quantity of hydrogen flowed out through the stethoscope.

The "Impure" Hydrogen (for Tables VIII and X).—The hydrogen was made by the 500-ampere electrolytic generator which is used in this Laboratory for preparing hydrogen for the liquefaction cycle. According to Latimer, Buffington and Hoenshel,[11] the hydrogen contains about 1% by volume of oxygen as it comes from the generator, but this oxygen changed to steam by passage through the nickel catalyst of those authors. Using their method, analyses were run for oxygen both before this research was begun, and after it was finished. In both cases about 0.01% by volume of oxygen was found, and part might well be due to imperfect removal of dissolved air from the solutions necessary. The hydrogen was passed through 100 cm. of glass tubing cooled with liquid air and through a plug of glass wool also kept at liquid air temperature. From this the hydrogen was kept flowing continuously through the resonance tube during measurements, and in fact for at least six hours before beginning them. When

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[11] Latimer, Buffington and Hoenshel, THIS JOURNAL, 47, 1571 (1925)

soldering had been done on the resonance apparatus, this was evacuated for at least twelve hours to evaporate the water from the soldering flux. It sometimes required six hours to pump out even most of this water, as indicated by a small manometer. Whatever parts of the system must be immersed in a liquid were carefully tested for leaks, using air presstire and immersing in water.

The "Pure" Hydrogen (for Table XI).—The purity of the above hydrogen cannot be guaranteed to better than 0.01% by volume. Because of the form of the relation between specific heat and velocity of sound, and because of the low density of hydrogen relative to air, an impurity of 0.01% by volume of oxygen or nitrogen amounts to 0.5% error in the specific heat, or to 0.0125 R. Accordingly, it was decided to repeat the measurements with hydrogen purified by passing through a glass spiral which was immersed in liquid hydrogen (using also the other glass spiral in liquid air as a preliminary). This new spiral contained a glass wool plug to collect air or other dust. The spiral was mounted in a hydrogen liquefier designed by Dr. W. F. Giauque of this Laboratory. The liquefier holds about 2 liters of liquid hydrogen, which permits measurements to be safely made for twelve hours. Some liquid is present even after twenty hours. The hydrogen used in the resonator was presumably never liquefied, but was certainly cooled to the condensing point since in the trap it was under slightly greater pressure than the liquid hydrogen in the surrounding container. As shown in Fig. 3, the specific heat results obtained below room temperature are only very slightly lower than those with hydrogen direct from the generator. In this new series the resonator was carefully evacuated for several days at a temperature higher than that used in the next run, using a Cummings mercury diffusion pump. In this way a few small leaks (otherwise practically undetectable) in the telephone chamber were detected and repaired from time to time, as they appeared, these being detected by the McLeod gage on removing the liquid from the thermostat. As previously explained, gas from the telephone cannot get into the resonator during specific heat runs; but it was found that, especially when the resonator was heated, a considerable amount of adsorbed gas (probably water) was given off, enough to account for the high results obtained above room temperature with "impure" hydrogen. We then check the statement of Latimer, Buffington and Hoenshel[11] that their nickel catalyst gives hydrogen better than 99.99% pure by volume. In this second series the resonator was never filled with hydrogen until measurements with the McLeod gage showed a rate of de-adsorption of gas which would not contaminate the hydrogen to as much as 0.001% by volume (taking into account the rate of flow of the hydrogen through the apparatus); at 100° this required several days of pumping.

The Air (for Table XII).—Runs were made with air at room temperature, to verify the Kirchhoff-Helmholtztube correction. To avoid variation from day to day, *all* the air to be used was pumped into a gas cylinder by our liquid air plant compressor, first blowing out the compressor for some time to avoid fractionation due to the air liquefier. As used, the air was bubbled through several towers of concentrated potassium hydroxide solution, through towers of concentrated sulfuric acid and finally through a 100cm. glass spiral cooled with solid carbon dioxide. Several feet of glass wool were installed in appropriate places in the line, and especially more than enough to eliminate the smell of sulfuric acid spray.

Air cannot be purified safely by passing through a liquid air trap. Fresh liquid air contains about 20% oxygen, but the gas evaporating from it contains about 5% oxygen.[12] Obviously if ordinary air is passed very slowly through a trap cooled by fresh

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[12] Dodge and Dunbar, THIS JOURNAL, 49,607 (1927).

liquid air, the gas emerging will contain 5% oxygen. This explains the supposedly surprising statement of Stock and Ritter[13] that the density of dried air varies from day to day over a range of 0.13%. Some measurements of ours (not given in this paper) on the velocity of sound in air purified by a liquid air trap indicated an even greater concentration of nitrogen than was found by Stock and Ritter. Moreover, Dr. M. Tamele of this Laboratory has found that carbon dioxide is not completely removed by passing air through a liquid air trap containing copper gauze unless at least some of the air is condensed, presumably thus wetting the carbon dioxide dust enough to allow it to stick to the gauze.

Oscillating Circuits.—The sound was produced by exciting the telephone ("T," Fig. 1) by radio apparatus. The telephone diaphragm must be tightly clamped to work at high frequencies without enormous distortion. In this telephone the hard rubber clamp was replaced by one of brass, as the rubber one becomes loose with large temperature changes. Presumably, using diaphragms of smaller diameter than ours of 1.75 inches, results could be obtained with frequencies higher than 12,000 cycles per second. This was not advisable, because the ear is not very sensitive to frequencies above 15,000 cycles, especially in recognizing changes in intensity. Also the ear shows a very great fatigue effect at such frequencies after listening for a few seconds.[14]

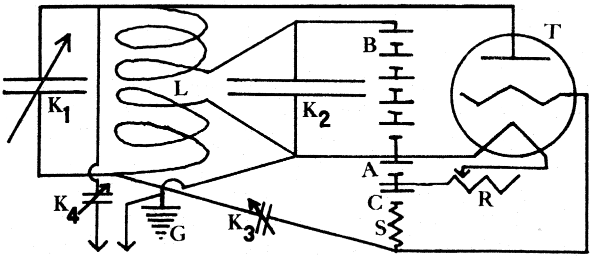

Fig. 2.—Oscillating circuit.

Two independent oscillating circuits are used, as should always be done when a constant frequency is desired; if the frequency of the circuit should begin to vary erratically, that is most easily noted by setting up beats between the two circuits.

The double inductances used in the two circuits for most of the measurements (L in Fig. 2) were of about 0.025 and 0 10 henries, respectively. Inductances were made from No. 21 wire, or wire larger in diameter, giving a low damping coefficient. Each inductance was in two approximately equal sections, for the "Hartley Circuit."

Small 3-electrode radio tubes were used for excitation. For constancy of frequency tungsten filaments were preferable to oxide filaments for the oscillator (not necessarily for the amplifier); the real requirement is probably a good vacuum in the tubes. A filament voltage of 2 to 5 volts heated the filament, battery "A" with rheostat " R being used. The grid was coupled through a small 3-plate variable condenser "K_3." Its capacity, and the filament voltage, should be somewhat, but not a great deal, larger than the minimum necessary; the plate voltage should not be excessive. Below 1000 cycles "K_3" was short-circuited by a switch. The negative grid "bias" was maintained by battery "C" and resistance "S" (500,000 ohms).

Except for occasional replacing of inductances, the frequency was controlled by capacity "K_1," which could be varied continuously from 3 to almost 0 μF.

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[13] Stock and Ritter, *Z. angew. Chem.*, 39,1463 (1926).

[14] See, however, a method by which the velocity of sound was measured at frequencies as high as 1,500,000 cycles per second, Pierce, ***Proc. Am. Acad. Arts Sci., 60,*** 271 (1924–1925).

K_2 was a 15 μF by-pass condenser for the B battery. K_2 was often disconnected altogether, as usually it did not affect the constancy or ease of production of osciliations.

The output energy was very small, passing through a 3-plate condenser K_4 similar to K_3. This lead, together with the battery ground, excited the amplifiers.

It is important that all electrical connections be tight. Switches were avoided except for filament rheostats. Trouble was often produced by screws in the 3-plate condensers or in the tube supports working loose. Also the spring clips in the tube supports must sometimes be sandpapered.

With precautions noted above, the "instantaneous" frequency of the circuits did not usually change by more than 1 part in 30,000 in half an hour, as shown by heat measurements. This was sometimes true even only an hour after charging the batteries, and applies to the range 200 to 12,000 cycles per second. Frequencies below 300 were sensitive to changes in battery voltage.

Except for Murdock variable air condensers for the fine adjustment, of total range 0.001 or 0.0005 μF each (sometimes filled with oil to double the range), the condensers K_1 have mica for dielectric. Some are ordinary radio condensers, each of capacity 0.005 μF or less, connected in parallel by binding posts. The layers of the radio condensers were tightly clamped with nuts and bolts. After clamping it was necessary to measure the capacities of the small radio condensers, using a Wheatstone Bridge. For each inductance a plot of frequency against capacity was made to hasten the adjusting of capacities. By using logarithmic plotting paper a straight line is obtained.

Measurement of the Frequency.—The frequency of the oscillating circuits was measured by comparison with a siren, using a beat method. It is not necessary for the siren to run at constant speed, as long as the beats do not come too fast to be counted. The siren disk had 80 or 20 holes in the rim. Through these air was blown by a jet operated at a pressure of 50 lb. per sq. inch or less. The disk was mounted on a motor with a maximum speed of 50 revolutions per second It was hard to make comparisons with the siren at frequencies higher than 6000 cycles, due to the preponderance of the noise of the driving motor over the high frequency. Accordingly, the main oscillating circuit is compared with the auxiliary one, whose frequency is almost $^1/_2$, $^1/_3$ or $^1/_4$ as great, by a beat method described below. Later the auxiliary circuit was kept at about the resonant frequency of the hydrogen (or at about twice the resonant frequency), which enormously speeded up the measurements, as only a few measurements on the siren were needed at each temperature, even when a large number of overtones was measured. The auxiliary oscillator operates a telephone near the siren, a radio tube providing amplification. This telephone was in a tight glass compartment from which a short glass tube led to an open end within 2 inches of the siren jet. The open end may be stuffed with cotton waste, the siren motor also being supported on rubber stoppers to drown out the noise of the motor. The siren note may be heard, for a cotton plug transmits more sound than can enter through the entire wall of the glass tubing.

Sound within the short glass tube is heard through a T-connection, using the ear pieces from a stethoscope. Thus any beats are easily heard and counted.

Besides the siren disk a 10-lb. flywheel is mounted on the motor. This shunt-wound, 0.5 horsepower D. C. motor was operated by a storage battery. After starting the motor, all resistance was cut out of the armature circuit. To obtain changes in speed, the armature voltage could be varied at will from 20 to 105 volts, in approximately 2-volt steps, by adding storage cells. The field was excited by the entire 105-volt battery, and fine adjustments of speed were obtained by a rheostat in series with the field coil. These precautions were necessary to obtain the required constancy and reliability in speed.

A second shaft is direct-connected to that of the motor by a short piece of rubber tubing, the rubber being prevented from slipping by wires through holes in the shafts. Thus, using a worm and gear, a disk is driven at a rate $^1/_{192}$ as fast as the siren disk.

For recording time on the two disks, we had two short, pointed No. 12 copper wires, one held near each disk. Either of the pointed wires could be connected at will to the secondary of an induction coil. The two disks are smoked by holding them in the flame of burning camphor, so that a spark mark made while the disks are moving may be located as a pinhole in the soot.[15]

A telegraph relay was actuated once a second by means of a chronometer in the Department of Astronomy. Tests showed the relay, together with our sparking system, to give two-second intervals to $^1/_{1000}$ second. The platinum contacts of the relay were in the primary circuit of the induction coil, which circuit could be finally completed by a knife switch so that sparks are not necessarily made whenever the relay moves. The relay had a set of contacts on each side of the moving arm, the second set operating a machine for counting seconds.

An actual comparison is made as follows:

Listening with the stethoscope, and with the proper armature voltage, the operator adjusts the field rheostat until the frequency of the siren is slightly above (or below) that of the telephone. This is noted by the slow beating between the two pitches of sound. The beats are then counted for a 120-second interval, there being between 200 and 600 beats during that time. At the start of the 120-second interval, that is, on the zero second, a spark mark is allowed to be made by the chronometer on the high speed siren disk. The sparking point near the disk is then shifted by means of a small electromagnet, and another spark mark is allowed to be made on the 120th second. On the No. 2 and No. 122 seconds, spark marks are made on the slow-moving disk. Here again an electromagnet allows the two spark marks to fall on circles of different radius, so that they may be distinguished from each other. The machine is stopped, and the spark positions measured. From the four positions, from the number of beats counted and from the whole number of revolutions of the slow-moving disk in 120 seconds (determined separately, usually between 5 and 25), the frequency of the telephone is calculated. If everything is working properly, a second comparison checks this to 0.10 cycle per second for frequencies around 3000 cycles per second. Frequencies less than 500 are checked to 0.01 cycle per second. The comparison must be made twice, because of the many chances for mistakes. The beats were occasionally double or triple, but measurements with the siren first above and then below the frequency of the auxiliary circuit eliminate any such uncertainty.

The "clock-fork" invented by Koenig many years ago gives frequencies *as* accurately as our siren; Miller[16] claims a possible accuracy of 1/650,000 for the frequency of his 60 to 70 cycle per second clock fork. However, for our purposes the siren has certain advantages of variability of pitch, ruggedness and quick operation.

Amplifiers.—Three amplifiers are used. The first is the radio tube which operates the telephone for comparison of the auxiliary oscillating circuit with the siren. The second amplifier was excited by the main oscillating circuit and consisted of two 7.5-watt stages, with two transformers. The output energy was regulated by the filament voltages. The output of this amplifier operates the telephone at the end of the hydrogen chamber, by which means stationary sound waves are set up in the hydrogen gas. A resistance repeating amplifier with 800 volts on plate[17] was tried in place of the transformer repeater but it did not increase the range of possible measurements to more than 14,000 cycles per second, while 12,000 cycles per second could be used with the trans-

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[15] See Encyclopedia Britannica, 11th ed., **6,** 303, for work of Sir Andrew Noble on bullet velocity.

[16] Miller, "Science of Musical Sounds," Macmillan Co., New York, **1916,** p. 40.

[17] Morecroft, "Principles of Radio Communication," John Wiley and Sons, Inc., **1921.**

former repeater. Because of the erratic character of the 3 determinations of velocity made using the resistance repeater (3 highest frequencies with tube No. 100A at 0°, see Table VIII), further work with it was abandoned.

The third amplifier was used for comparing the main and auxiliary oscillating circuits with each other. Three radio tubes were used. One was excited by the auxiliary circuit, one by the main circuit (through the output of the second amplifier) and both of these tubes induce into the third tube by means of a transformer. (Where the frequency of the main circuit is many times that of the comparison circuit, this third tube must be replaced by a 3-tube amplifier.) The last tube operates a pair of headphones, so that any beats may be heard. The auxiliary oscillator had approximately $^1/_2$ or $^1/_3$, etc. (the numerator of the fraction being 1 or occasionally 2), the frequency of the main oscillator. Calling this fraction x/n (where x/n is reduced to its lowest terms), the auxiliary frequency v and the main frequency $nv/x \pm d$, xd beats per second are usually heard in the headphones of the third amplifier, due to "distortion."[4a] A suitably small, variable condenser formed part of K_1 in the auxiliary oscillator and, by moving this, it could be found whether d was positive or negative. This condenser was fitted with a stop so that it could be brought to either end of its range but have a reproducible capacity at those two positions. From the measured difference of capacity between the ends of this range, together with the approximate frequencies of the two oscillating circuits and the value of K_1 in the auxiliary circuit, we may calculate the change in d when the small variable condenser is moved from one end of its range to the other. If now we measured the difference in the number of beats per second in the headphones for the two positions of this condenser, this was found almost always to agree with the calculated value. In a *very* few cases, however, this number of beats was exactly half (not twice) the calculated number; also, both types of beats were sometimes heard at once.

When the *difference* in the numbers of beats was a *multiple* of the calculated difference, or if the *total* number of beats was very large, a spurious maximum was being used. Obviously these tests are most reliable if the auxiliary circuit is kept at the resonant frequency of the hydrogen.

Accordingly, the auxiliary and main circuits were compared by counting the number of beats produced by the third amplifier in a definite time (25 sec.), with the above condenser at one end of its range, and by determining the sign of this beat difference, from the effect of moving the condenser.

Maintenance of Temperatures (see Fig. 1).—The resonator and its telephone were immersed in a stirred liquid-bath contained in a 180 cm. long Dewar tube (D_2). The stirrer propellor was so efficient that when this Dewar was filled with water and a 5cm. layer of crushed ice was maintained at the top, the temperature difference between top and bottom dropped to 0.003° in about thirty minutes; but the behavior of this thermostat was discussed in the section on "calibration of thermocouples." For work at lower or higher temperatures than that of the room, a liquid bath was maintained in a larger Dewar (D_1) outside the first one.

The larger Dewar was made from a steel tube 9 inches in diameter and 220 cm. long, and an inner tube of sheet Monel Metal 6 inches in diameter. The space between the walls and between the bottoms was filled with silk floss and a vacuum of about 0.003 mm. or better maintained by continuous pumping with a Cummings mercury vapor pump and a liquid air trap. A leak prevented a better vacuum. (This was later remedied by replacing the Monel Metal tube by a brass tube.) The pressure sometimes rose to between 0.01 mm. and 0.02 mm., due to various causes, and this increased the heat leak into the outer bath by a factor of 3 or 4. The 6 inch sheet Monel tube was made by folding and riveting a flat sheet of the metal and soldering. Considerable trouble was found due to vacuum leaks around the soldered rivets. Dr. W. F. Giauque of this Laboratory found that this trouble could be avoided by using Monel Metal rivets in place of rivets of galvanized iron. At the lower temperatures the outer bath warmed about 2° per hour.

The lower end of the outer tube was threaded so that an ordinary 9-inch pipe cap could be screwed on (see "F" in figure). Gas leakage past the threads was prevented by de Khotinsky cement.

The smaller Dewar was made from brass tubing. For about 20 cm. from the top, the inner piece of brass tubing was replaced by a German silver tube (thickness 0.01 inch) for reducing heat leak. The diameters of the walls were 3.5 and 2.75 inches. A vacuum of 10^{-5} mm., or better, was maintained by continuous pumping, using a liquid air trap as well.

At first a 180cm. silvered Pyrex glass Dewar was used in place of the brass one, many of the measurements being made with it. However, two such Dewars were lost by breakage, due in at least one case to the giving way of strains and not to mechanical shock. The metal Dewar gave a somewhat greater heat leak at the top than the glass one but the vacuum in the metal Dewar could always be read.

For all work where water or liquid air or oil (heated electrically) were not used for the baths, petroleum ether was used. This was cooled by immersing in it large test tubes (with a 2-liter baffle at the top), to hold liquid air.

Thermal Expansion of Brass.—In velocity of sound determinations other than at room temperature, it is necessary to know the thermal expansion of the apparatus. Buffington and Latimer[7] measured the coefficients of expansion of copper and aluminum over the required temperature range and, accordingly, the coefficient of expansion of the brass sound tube No. 150A was measured relative to both copper and aluminum. For this purpose, three aluminum rods 0.25 inch in diameter barely projected out of the smaller Dewar, which was nearly filled with an appropriate stirred liquid bath, with a thermocouple for measuring the temperature. A scratch was made on each of the three aluminum rods and the heights of these scratches measured at various temperatures, by means of a cathetorneter, after scraping off the atmospheric ice. One of the aluminum rods was short and was soldered to the top of the brass resonance tube. Another much longer aluminum rod was soldered near the bottom of the brass tube. The third aluminum rod was short and was soldered to a long copper rod, the other end of the copper rod being soldered to the bottom of the brass tube. The relative motion of the scratches gave the relative thermal expansions of brass, copper and aluminum, for bending of the rods was prevented. In Table IV are given the results; either series is probably accurate to 0.1 mm. A graph was used for the velocity of sound calculations. The uncertainties which are evident are due to us and not to Buffington and Latimer.

TABLE IV

LENGTH OF A 100CM. BRASS TUBE RELATIVE TO ITS LENGTH AT 273.1°K

Abs. *temp., °K.*	From *copper data, mm.*	From aluminum *data, mm.*	Average
273.1	0.00	0.00	0.00
254.1	− .32	− .39	− .36
236.3	− .57	− .68	− .63
218.3	− .93	− .95	− .94
196.3	−1.31	−1.35	−1.33
174.4	−1.67	−1.71	−1.69
157.2	−1.93	−1.97	−1.95
151.6	−2.00	−2.06	−2.03
81.7	−3.05	−2.92	−2.98

For work above 0°, the coefficient of expansion of brass was obtained from tables.[18]

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[18] *Scientific Papers, U. S.* Bureau of Standards, 17, 110 (1922).

Calculation of Specific Heat from Velocity of Sound at a Given Temperature

In this section all quantities except pressure are taken in absolute, C. G. S. units.

R = Gas constant (ergs per degree per mole).
P = Pressure (dynes per sq. cm.).
p = Pressure (atmospheres).
V = Volume of 1 mole of substance (cc.).
M = Molecular weight of substance and number of grams in 1 mole.
T = Absolute temperature.
C_p = Specific heat at constant pressure (ergs per degree per mole).
C_v = Specific heat at constant volume (ergs per degree per mole).
W = Velocity of sound (cm. per sec.).
S = Entropy of substance (ergs per degree per mole).

Other quantities are defined as needed.

Many years ago Sir Isaac Newton showed that

$$W = \sqrt{-\frac{V^2}{M}\cdot\frac{\partial P}{\partial V}} \qquad (1)$$

for a gas or liquid or for longitudinal waves in a solid. Assuming the process to be reversible and adiabatic, the entropy of any part of the gas is constant, or

$$W = \sqrt{-\frac{V^2}{M}\left(\frac{\partial P}{\partial V}\right)_S} \qquad (2)$$

As[19]

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P \text{ and } C_v = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$W = \sqrt{-\frac{V^2}{M}\left(\frac{\partial P}{\partial V}\right)_T\frac{C_p}{C_v}} \qquad (3)$$

Also[20]

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T \qquad (4)$$

As the equation of state of hydrogen at low pressure, we will take

$$PV = RT + \frac{a}{V} \qquad (5)$$

where a is a function of T, but not of P or V. This equation, or one equivalent to it, was used by Kamerlingh Onnes and his staff for calculating the relation between the hydrogen and thermodynamic temperature scales.[21]

Solving (5) for P, and differentiating

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V^2}\left[RT + \frac{2a}{V}\right] \qquad (6)$$

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[19] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 132.

[20] Ref. 19, p. 136.

[21] See, for example, Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, No. 97b, p. 34, where it is shown that the form of this equation of state introduces an error not larger than 0.0003° in the hydrogen scale at as low a temperature as 56°K., although his total correction to change to the thermodynamic scale amounts to 0.076° at this temperature.

Also, dividing (5) by P, and differentiating

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{P}\left[R + \frac{1}{V}\frac{\mathrm{d}a}{\mathrm{d}T} - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P\right]$$

Solving this for $\left(\frac{\partial V}{\partial T}\right)_P$, and substituting for P its value from (5)

$$\left(\frac{\partial V}{\partial T}\right)_P = V\frac{R + \frac{1}{V}\frac{\mathrm{d}a}{\mathrm{d}T}}{RT + \frac{2a}{V}} \tag{7}$$

If, now, we eliminate C_p between (3) and (4), solving for C_v, and substitute for the partial derivatives their values given by (6) and (7)

$$C_v = T\frac{\left[R + \frac{1}{V}\frac{\mathrm{d}a}{\mathrm{d}T}\right]^2}{MW^2 - \left[RT + \frac{2a}{V}\right]} \tag{8}$$

This equation gives C_v at p atmospheres if the velocity of sound is measured at that pressure. Supposing the experiment to be carried out at a pressure of p atmospheres and writing C_{v_0} for the specific heat of the substance at zero pressure, we have first[22]

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \tag{9}$$

Now by dividing (5) by V and then differentiating twice, we have

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{1}{V^2}\frac{\mathrm{d}^2a}{\mathrm{d}T^2}$$

Substituting this value for the second derivative in (9), we may integrate

$$C_v - C_{v_0} = \int_{P=0}^{P=p\text{ atm.}} \frac{T}{V^2}\frac{\mathrm{d}^2a}{\mathrm{d}T^2}(\partial V)_T = T\frac{\mathrm{d}^2a}{\mathrm{d}T^2}\int_{P=0}^{P=p\text{ atm.}} \frac{(\partial V)_T}{V^2} = \frac{-T}{V}\frac{\mathrm{d}^2a}{\mathrm{d}T^2} \tag{10}$$

Now the terms involving a in (8) and (10) are so small that we may write $1/V = P/RT$ in them without appreciable error for pressures of 1 atmosphere or less. We also expand the square in the numerator of (8) and neglect the second order term involving $(1/V)^2$. Then, if (8) and (10) are combined, eliminating C_v, and solving for C_{v_0} we obtain finally

$$\frac{C_{v_0}}{R} = \frac{R\left[T + \frac{2P}{R^2}\frac{\mathrm{d}a}{\mathrm{d}T}\right]}{MW^2 - R\left[T + \frac{2aP}{R^2T}\right]} + \frac{P}{R^2}\frac{\mathrm{d}^2a}{\mathrm{d}T^2} \tag{11}$$

We may remark that the R on the left-hand side of equation (11) may be taken in any units in which we wish to have C_v expressed; the R's on the right side of the equation must be in absolute c.g.s. units.

The data of state for hydrogen gas at pressures of 1 atmosphere or less are expressed by Onnes and Braak as values of B'_T at various temperatures.[23]

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[22] Ref. 19, p. 141.

[23] Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, No. 101b, p. 16; *Verslag. Akad. Wetenschappen Amsterdam, 1907,* p. 427.

B'_T is defined by the equation[24]

$$pv = A_T\left[1 + \frac{B'_T}{v}\right]$$

Here p is the pressure in atmospheres and we will write $P = bp$, b being the number of dynes per sq. cm. in 1 atmosphere. A_T is defined as $T/273.10$ and v is the volume divided by the "theoretical normal volume." As the latter volume is, for 1 mole, $273.1\ R/b$ cc., we have $v = bV/273.1\ R$. The Leiden equation of state may then be written in c.g.s. units as

$$PV = RT + \frac{273.1\ B'_T\ R^2T}{bV} \tag{12}$$

Comparing this with equation (5), we see that

$$a = \frac{273.1\ R^2T\ B'_T}{b} \tag{13}$$

Considering again equation (11), we see that it involves three correction terms, each involving P to the first power. Expressing now the pressure in atmospheres, (11) may be written

$$\frac{C_{v_0}}{R} = \frac{R(T + Yp)}{MW^2 - R(T + Xp)} + Zp \tag{14}$$

and it follows that

$$\begin{aligned} X &= \frac{2ab}{R^2T} = 546.2\ B'_T \\ Y &= \frac{2b}{R^2}\frac{da}{dT} = 546.2\ \frac{d(T\ B'_T)}{dT} \\ Z &= \frac{b}{R^2}\frac{d^2a}{dT^2} = 273.1\ \frac{d^2(T\ B'_T)}{dT^2} \end{aligned} \tag{15}$$

Merely for convenience, we define a new quantity Δ such that

$$B'_T\ 10^3 = 1 - \frac{110}{T} + \Delta \tag{16}$$

In Table V are given values of Δ at the temperatures of the measurements of Onnes and Braak,[23,24] as well as their values of B'_T.

TABLE V

HYDROGEN DATA OF STATE

Abs. temp.. °K.	$1 - \frac{110}{T}$	$B'_T\ 10^3$	$\Delta \cdot 10^3$
373.10	+0.705	+0.6321	−0.073
293.10	+ .625	+ .622	− .003
273.10	+ .597	+ .5807	− .016
169.55	+ .351	+ .394	+ .043
133.25	+ .174	+ .229	+ .055
109.00	− .009	+ .018	+ .027
90.34	− .218	− .241	− .023
77.89	− .412	− .432	− .020
68.47	− .606	− .692	− .086
60.36	− .822	−1.009	− .187
55.77	− .972	−1.203	− .231

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[24] Onnes and Braak, *Comm. Phys. Lab. Univ. Leiden*, No. 97b, p. 33; *Verslag.* Akad. *Wetenschappen* Amsterdam, 1907, p. 668.

Equations (15) may now be written in the form

$$\begin{aligned} X &= 0.5462\left(1 - \frac{110}{T} + \mathrm{A}\right) \\ Y &= 0.5462\left(1 + \frac{\mathrm{d}(T\Delta)}{\mathrm{d}T}\right) \\ Z &= 0.2731\left(\frac{\mathrm{d}^2(T\Delta)}{\mathrm{d}T^2}\right) \end{aligned} \qquad (17)$$

We have plotted A from Table V, drawing the best curve. From this curve values of A and hence of X may be obtained at 10° intervals, from which Y could be obtained. Similarly, by again differentiating these slopes, we may obtain Z. The slopes found were smoothed out by plotting them directly against T (see Table VI).

For comparison we give Table VII, calculated from Berthelot's equation of state, using a critical pressure of 12.8 atmospheres and a critical temperature of **33.1°K.** Use of the actual critical volume in this equation gives poorer agreement with Table VI.

TABLE VI

VALUES OF CORRECTION TERMS IN EQUATIONS (14), (18) AND (21), FOR HYDROGEN, FROM DATA OF ONNES AND BRAAK

Abs. temp., °K.	X, °/atm.	Y, °/atm.	Z, per atm.	$t°$, °/atm.
373	+0.345	+0.41	?	−0.019
300	+ .332	+ .427	−0 00022	− .008
270	+ .318	+ .440	30	+ .000
250	+ .307	+ .455	36	+ .006
200	+ .262	+ .496	53	+ .021
150	+ .175	+ .561	77	+ .039
100	− .049	+ .659	107	+ .067
90	− .121	+ .683	112	+ .073
80	− .227	+ .710	118	+ ,080
70	− .356	+ .741	...	+ .087
60	− .497	...	...	+ .096

TABLE VII

SAME AS TABLE VI, CALCULATED PROM BERTHELOT'S EQUATION

Abs. temp., °K.	X, °/atm.	Y, °/atm.
Infinite	0.364	0.364
300	.327	.391
200	.304	.424
100	.125	.603
70	− .123	.851
60	− .289	1.017

An equation of state of Keyes[25] requires that $Z = 0$, and hence that C_v is independent of pressure. But Table V shows that A has a second derivative different from zero; in any case, the Z term is less than the experimental errors of this research.

In Table VI we give $t°$, the correction for giving the temperature scale

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[25] **Keyes, Townshend and Young, J.** *Math. Phys.,* Mass. *Inst.* Tech., 1,251 (1922).

in terms of the absolute scale. In the constant volume hydrogen thermometer, if T be any temperature, J the corresponding pressure of the hydrogen in atmospheres and J_0 the pressure when $T = 273.1$°K., we define t° as follows

$$T = 273.10\,\frac{J}{J_0} + t^\circ J_0 \tag{18}$$

We may calculate t° from equation (12). In the correction term of that equation we may write

$$V = \frac{Pv_0}{273.1\ R} = \frac{b\ J_0}{273.1\ R}$$

which gives for the equation of state of the thermometer gas

$$PV = RT\,(1 - B'_T\,J_0)$$

Equating the hydrogen volume at T with that at 273.1°, we obtain, neglecting second order corrections

$$T = 273.1\,\frac{J_0}{J} + T(B'_{273.1} - B'_T)\,J_0$$

that is

$$t^\circ = T\,(0.5807\cdot10^{-3} - B'_T) \tag{19}$$

We may put Keyes' hydrogen scale correction in the form[26]

$$t^\circ = 0.055^\circ\left(1 - \frac{T}{273.1}\right) \tag{20}$$

This agrees with Table VI at 273.1°K. Also, at 373.1°K., Equations (20) and (19) differ by only 0.001°, for Keyes, Townshend and Young picked the 0.055° with that very purpose in mind. However, (20) requires that t° should not become greater than 0.055" at low temperatures, but the values of t° in Table VI become considerably greater.

Referring to Equation (14) for our measurements we take p = 1 atmosphere, not bothering to read the barometer at any time. We have also R = 8.316 × 10^7 ergs per degree,[27] and for the molecular weight of hydrogen M = 2.01554 g. per mole.[28] Our final equation for the calculation of the specific heats of hydrogen is, then, from (14)

$$\frac{C_{v_0}}{R} = \frac{T + Y}{2.42369 \times 10^{-8}W^2 - T - X} + Z \tag{21}$$

T being the absolute temperature of the measurement and W being in cm. per mean solar second.

Effect of the Tube on the Velocity of Sound

When hydrogen is confined in a tube, the velocity of sound is less than in the free gas. This decrease in velocity is almost entirely due to the walls of the tube, rather than the ends, if the tube is very long. The effect of the walls is given by the formula of Kirchhoff and Helmholtz[29]

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[26] Keyes, Townshend and Young, ref. 25, p. 295, and equation 11, p. 251.

[27] Ref. 19, p. 60.

[28] Moles, *Z. physik. Chem.*, **115**, 61 (1925); **117**, 157 (1925); *Anales españ. fís. quím.*, 23, 39 (1925); THIS JOURNAL, 48, 552 (1926).

[29] Kirchhoff, *Pogg. Ann.*, **134**, 177 (1868).

(Equation 22). Many observers have said that this formula gives too small a correction,[30] but their work involves tubes containing a large amount of dust. The correction affects our specific heats by about 2%, but in some work of Partington and Shilling[31] an incorrect application of this correction makes their gas specific heats at high temperatures too low by about 13%. This is because they use a tube correction 9 times too great. These observers claim an accuracy of 1%. The only plausible explanation of their high results seems to be that they did not carefully measure their frequency, for they used a "standard wave meter." Making that explanation, a recalculation of Partington and Shilling's data for air at 1073°K. gives C_p as 7.87 cal. per mole per degree, while Lewis and Randall[32] estimate 7.57, and Partington and Shilling give **7.222.** Assuming Partington and Shilling to have the correct frequency, we obtain 8.17. These calculations were only made roughly.

The holes in the ends of our resonators were 1 mm. in diameter as with Grüneisen and Merkel; however, ours were 1 mm. long as well. The careful work of Grüneisen and Merkel[4b] indicated that with air at 0°, the end openings have very little effect. With hydrogen, the end openings might be much greater, because of the ability of hydrogen to be easily blown through small openings. In the case of regular, viscous flow, we find that since the viscosity of hydrogen is about half that of air,[33] only twice as much energy will be lost through the end openings with hydrogen as with air. If then the flow is not at all turbulent, the end correction amounts to about twice the percentage of the velocity of sound with hydrogen as with air (for the same frequency); accordingly we ignore any end correction. The purpose of using tubes of different lengths was to measure the end correction, but it was found, as also noted by Grüneisen and Merkel, that with hydrogen the end correction is less than the error of experiment.

Because of the importance of the wall correction, a large number of measurements (Table VIII) were made at 0° (although with "impure" hydrogen), so that a more or less reliable estimate of that correction could be made. Each value of Table VIII represents the mean of six determinations. The Kirchhoff-Helmholtz relation requires that the tube correction be inversely proportional to the square root of the frequency, but the range of frequency over which the velocity of sound can be measured accurately in hydrogen is not sufficient to test that (see Equation 22). Moreover, our source of sound was probably not a pure sine vibration.

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[30] (a) Stürm, *Ann. Physik.*, 14, 822 (1904); (b) Seebek, *ibid.*, 139, 104 (1870); (c) Kayser, *ibid.*, 2,218 (1877); (d) Muller, *ibid.*, 11,331 (1903).

[31] Partington and Shilling, *Trans. Faraday Soc.*, 18,386 (1923).

[32] Ref. 19, p. 80.

[33] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, 1923, Vol. I, p. 171; 1923, Vol. II, p. 1274, 1277, 1304.

TABLE VIII

VELOCITY OF SOUND IN HYDROGEN IN VARIOUS RESONATORS AT 0° (273.1°K.)

In meters per second (equations in this paper refer to cm. per sec.). Fundamental counted as first overtone. "Impure" hydrogen. Not corrected for effect of tube.

Tone no. .	Tube 150A	Tube 150B	Tube 100A	
8	....	....	1256.6	
9	....	....	1257.6	
			1256.9	
10	1256.2	....	1256.9	
11	1256.8	....	....	
12	1256.4	1254.0	1258.1	
13	1256.7	1257.4	1257.9	
	1257.5			
14	1257.1	1254.9	1257.8	
15	1256.8	1255.3	1257.4	
16	1256.6	....	1258.0	
	1256.9			
17	1257.4	1254.2	1257.5	
18	1257.3	1255.7	1258.4	
19	1257.6	1253.8	1257.8	
			1258.2	
20	....	1255.1	1258.3	
21	1256.7	1253.2	1258.3	
		1254.7		
22	1256.7	1253.2	....	
23	1257.0	....	....	
24	1258.4	1256.2	....	
25	....	1255.3	....	
26	1256.1	1256.1	....	
	1256.1			
27	1256.6	....	....	
28	1257.0	1252.0	....	
Mean	1256.95	1255.0	1257.8	**(Certain values not considered)**

Grüneisen and Merkel found, by taking average results of the 8th to the 16th or 17th overtones, a velocity of sound of 1258.9 m. per sec. for a 5cm. diameter tube, and 1256.5 m. per sec. for one of 2.6 cm. diameter. Assuming an inverse diameter law, this gives a correction of about 2.6 m. per second for the 5cm. tube, and a corrected velocity of 1261.5 m. per sec. Their wider tube was about 95 cm. long and the narrower one about 79 cm. The range of frequency is from about 5000 cycles per sec. to 12,000. For our own data, this same method of calculation was tried; from our 150cm. tubes (Table VIII) we obtain 1258.9 meters per sec. (Later results with "pure" hydrogen give 1260.75 m. per sec.) Grüneisen and Merkel believe their best value to be 1260.2, but their method of calculation consists in making a rather doubtful comparison with the tube correction for air.

In Table VIII it was not considered necessary to give the frequencies, these being converted into velocity by dividing by the number of the overtone and multiplying by twice the inside length of the tube in question. The three highest frequencies used for tube 100A were amplified with the resistance repeater and not considered in the average. The overtones below No. 11 in the longer tubes, or below No. 8 in the shorter tube, were not sharp or well defined. The dashes in the table are overtones which could not be measured accurately because some other maximum, due to the brass apparatus or perhaps to hydrogen in the telephone chamber, was close to the overtone wanted. In some cases disturbing maxima could be eliminated by using a lower intensity of sound in the telephone. If an unnecessarily large current was fed into the telephone, disturbing maxima appeared, or the true maximum became less well defined.

We need the tube correction for a 4.8cm. diameter tube at **all** temperatures used. From Table VIII we obtain **1256.95–1255.0,** or **1.95** meters per second for 0°. Combining with the **2.5** m. per sec. of Griineisen and Merkel for 0°, an average of **2.2** meters per second is to be used for 0°. If we write W for the velocity of sound, S for the density of the gas, n for the coefficient of viscosity, j for the heat conductivity, v for the frequency and D for the diameter of the tube, then the Kirchhoff-Helmholtz value for the tube correction *AW* is, using absolute c.g.s. units (except that any consistent energy unit may be used for C_p, C_v and j),[29]

$$\frac{\Delta W}{W} = \frac{1}{D\sqrt{\pi v S}}\left\{\sqrt{n} + \left[\sqrt{\frac{C_p}{C_v}} - \sqrt{\frac{C_v}{C_p}}\right]\frac{j}{C_v}\right\} \tag{22}$$

For $0°$, we take D = 4.8 cm., v as 7000 cycles per second as a rough mean value of the frequencies used, and obtain from equation **(22)** $\Delta W/W = $ **0.00185.** About three-fourths of the correction is due to viscosity and the other one-fourth to heat interchange between the walls and the gas. The experimental value of the correction, quoted above, gives $\Delta W/W = 2.2/1259.3 =$ **0.00175.** The agreement is close, and it **was** decided to use theoretical values for the Kirchhoff-Helmholtz correction.

TABLE: IX

KIRCHHOFF-HELMHOLTZ CORRECTION FOR HYDROGEN IN A TUBE OF 4.8 CM. DIAMETER

Observed velocity of sound is too low by percentage in table, at frequency of 10,000 cycles per second.

Abs. temp., °K.	Correction, %	Abs temp., °K.	Correction, %
373.1	0.191	100	0.075
273.1	.155	50	.063
250	.144	SAME FOR AIR	
200	.122	298	0.0476
150	.0995		

In Table IX are given the values of $\Delta W/W$ for various temperatures. The values of heat conductivity, viscosity and C_v were taken from Landolt-Börnstein.[33] A curve was plotted to make interpolation easy.

The values are for 10,000 cycles per second but the correction varies inversely as the square root of the frequency.

To settle finally the correctness of the Kirchhoff-Helmholtz correction, a wide tube 9.87 cm. in diameter was made (No. 168, Table III). Measurements at room temperature (Table XI, at 294.27°K.) were made with "pure" hydrogen and the specific heat was calculated. As seen in Fig. **3,** this point falls nearly on the curve. The effect of the correction is to lower the specific heat by about 0.017R while results in Tube 150A at about the same temperature are lowered by about 0.035R, a difference of 0.018R; but Fig. **3** shows a deviation of much less than 0.018R. This is more obvious if the specific heats of Table XI near room temperature are plotted on a larger scale. The total evidence for the correctness of Kirchhoff and Helmholtz is overwhelming.

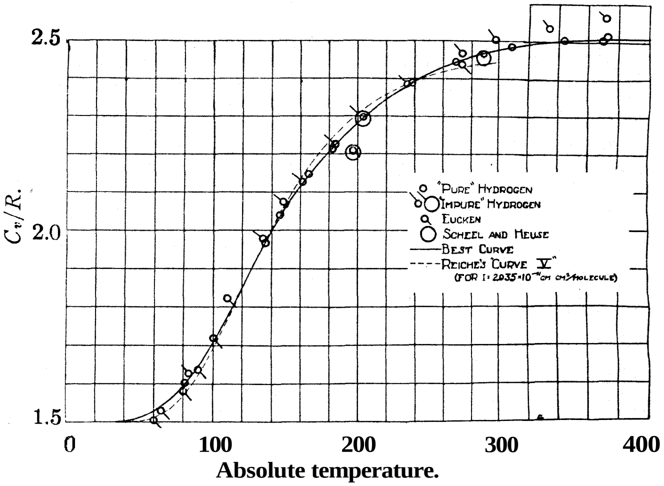

Fig. 3.—Specific heat of hydrogen.

Griineisen and Merkel concluded from their own data that the Kirchhoff-Helmholtz formula holds for air, but we also made runs with air at room temperature (purified as already stated). The difference between the tube corrections is not much more than the experimental error, and the results of Table XII check the Kirchhoff-Helmholtz formula to a fortuitous degree, although the three runs of the table each represent the mean of about 50 determinations. For reducing the air results to the same temperature, it was assumed that the velocity of sound is proportional to $\sqrt{T}$ over the small temperature range in question. For 24°, we obtain 34,566 cm. per sec. as the velocity of sound in free air.

Determination of Velocity of Sound and Specific Heat

For the Griineisen and Merkel data at 0°, it is best to ignore their narrow tubes. Applying the theoretical tube correction to the data from their largest tube, we obtain 126,115 cm. per sec. while our best curve (Fig. 3) gives 126,075. Either of these values is preferable to the value 126,020 cm. per sec. which Grüneisen and Merkel estimate from their own data. A mean of 126,090 cm. per sec. is probably the best value.

The measurements of velocity of sound at each temperature other than 0° consisted, both with "impure" and with "pure" hydrogen, of five or more different overtones, each overtone being measured at a slightly different temperature due to temperature drift of the thermostat. For each overtone the variable condenser of the main oscillating circuit was set at the maximum of sound about 6 times successively. The frequency was noted each time by beat comparison (for 25 seconds) with the very constant auxiliary oscillating circuit. Accordingly, for every temperature in the tables, from 30 to 60 independent measurements are averaged together.

The data are fairly consistent. For each of the temperatures used the values of the fundamental resonant frequency are usually the same, as given by the various overtones, within 0.1% or less. Moreover, the various measurements of a given overtone usually agreed among themselves to 0.1% or less. With air the agreement was to about 0.03% or less. For brevity the actual data are omitted. To take account of temperature drift during the various series, a single plot of e.m.f. of thermocouple against frequency was made and the slopes were read off the curve for each temperature in question. We thus may obtain the several values for the fundamental, reduced to the same mean temperature. While this method of calculation obviously gives the same result as a simple average (even if the wrong slope is read from the curve), yet it makes possible the elimination of a few slightly displaced maxima. These displacements and their cause are discussed above.

TABLE X

SPECIFIC HEAT OF HYDROGEN AT CONSTANT VOLUME IN TERMS OF THE GAS CONSTANT. VELOCITY OF SOUND IN UNCONFINED HYDROGEN

("Impure" hydrogen, Tube 150A)

Abs. temp., °K.	Velocity of sound, cm./sec.	C_v/R	From tones	Fundamental, per sec.
371.55	146,040	2.564	No. 13 to 17	484.96
333.51	138,590	2.536	14 to 18	460.62
297.79	131,200	2.505	16 to 19	436.41
273.10	125,920	2.467	10 to 28	419.07
234.77	117,210	2.387	19 to 23	390.50
203.63	109,830	2.294	19 to 24	366.10
184.57	105,040	2.228	16 to 21	350.23
161.58	99,030	2.128	22 to 27	330.39
148.00	95,210	2.076	18 to 23	317.70
133.89	91,280	1.979	21 to 25	304.70
83.52	74,640	1.628	18 to 22	249.36

TABLE XI

SPECIFIC HEAT OF HYDROGEN AT CONSTANT VOLUME IN TERMS OF THE GAS CONSTANT. VELOCITY OF SOUND IN UNCONFINED HYDROGEN

(Pure hydrogen, Tube 150A)

Abs. temp., °K.	Velocity of sound, cm./sec.	C_v/R	From tones	Fundamental, per sec.
372.52	146,630	2.516	No. 10 to 20	486.84
369.40	146,110	2.504	10 to 19	485.12
333.31	138.930	2.505	13 to 17	461.36
308.96	133,770	2.486	13 to 18	444.80
294.27	130,710	2.466	10 to 25	388.23[a]
269.02	125,150	2.444	10 to 20	486.84
238.23	118,170	2.390	16 to 26	393.61
203.63	109,900	2.298	14 to 24	366.30
182.41	104,630	2.213	14 to 23	348.87
165.58	100,160	2.147	18 to 27	334.12
145.64	94,715	2.041	15 to 20	316.03
135.71	92,000	1.967	15 to 23	307.05
81.12	73,800	1 6015	17 to 23	246.55

[a] Tube 168 used.

In Tables X and XI are given the velocity of sound and the specific heat. The velocity was found by multiplying the fundamental frequency by twice the length of the tube, applying the corrections for thermal expansion (Table IV) and the Kirchhoff-Helmholtz correction (Table IX). The specific heat was then calculated from Equation (21), using Table VI.

The results of Table XI for the velocity of sound and for the specific heat are believed to be correct to about 0.1 and 0.5%, respectively, but an extra decimal place is added. The result of Table XII for the velocity of sound in air at room temperature is believed to be good to 0.01%. All values are for 1 atmosphere pressure, but the specific heats at zero pressure may be found by merely adding algebraically the Z of Table VI; this effect is never more than 0.001.

TABLE XII

VELOCITY OF SOUND IN DRY CARBON DIOXIDE-FREE AIR AT ROOM TEMPERATURE

Series	Tube	Overtones	Abs. temp., °K.	Velocity (in tube), m./sec.	Velocity at 296.324°K., m./sec.
1	150A	No. 37 to 44	298.60	346.276	344.959
2	150A	45 to 56	296.324	345.009	345.009
3	168	30 to 40	296.237	345.019	345.070

Series	Mean Kirch. Helm. corr., m./sec.	Velocity of sound in free air, m./sec.
1	0.242	345.201
2	.216	345.225
3	.137	345.207
		Av., 345.21

Velocity at 24° in dry, carbon dioxide-free air = 345.66 meters per sec.

For the purpose of comparison, the results of some other observers are plotted in Fig. 3, as well as our own results. Also, Reiche's[2b] "curve V" is given, assuming a moment of inertia 2.035×10^{-41} gm. cm.^{2} per molecule.

Relation of Results to Quantum Theory

All quantum theories of rotational specific heat assume various states in which the number of molecules is proportional to $Pe^{-E/RT}$, where P is the "probability" of the state, e the base of the natural system of logarithms, E the energy of the state and RT the gas constant times the absolute temperature.

G. N. Lewis suggests the following graphical method of attacking the data. At low temperatures only the first two states have appreciable weight. Hence, writing now E for the energy difference between these two states, we have for the rotational heat content, H_r

$$H_r = PEe^{-E/RT}$$

as the limiting law for low temperatures. Differentiating, and writing $dH_r/dT = C_r$, we may easily show (using common logarithms)

$$\log (T^2C_r/R) = \log (PE^2/R^2) - E/2.303\,RT \tag{23}$$

Accordingly, by plotting log (T^2C_r/R) against $1/T$, the equation of the limiting straight line for low temperatures gives us both E and P. This was done, and from the "impure" hydrogen we obtain $E = 1003$ cal./mole and $P = 1.48$. The "pure" hydrogen gives $E = 1035$ cal./mole and $P = 1.51$ (see below, however).

These values for P are less than 2. Most theoretical equations proposed previously make P 2 or more. One of the best of such equations is curve V of Reiche, which gives $E = 1160$ cal./mole and $P = 2$, and which is shown for comparison in Fig. **3** (assuming moment of inertia 2.035×10^{-41} gm.cm.^{2}/molecule). E independently of P determines the moment of inertia; we obtain for the moment of inertia 0.742×10^{-41} $(n_2^2 - n_1^2)$ gm.cm.^{2}/molecule, assuming quantum numbers n_1 and n_2 for the first two states, and E as 1060. cal./mole. We may remark that all theoretical equations *must* lead to about the same value for the first energy jump; differing moments of inertia are due to use of different quantum numbers.

A recent specific heat equation due to Dennison[34] fits our data extremely closely below 250°K. It gives lower values than ours above 250°K., as might be expected if stretching of the molecule at high rotational speeds is ignored. He assumes a moment of inertia, 4.64×10^{-41}, but the fit is better with 4.75×10^{-41}. At this moment of inertia we find $n_2^2 - n_1^2 = 4.75/0.742 = 6.4$. To get such a large value theoretically Dennison could assume a large quantum number for the zero state, but he rather assumes two independent series of quantum numbers $^1/_2$, $^5/_2$, $^9/_2$, $^{13}/_2$, ... and $^3/_2$, $^7/_2$, $^{11}/_2$, $^{15}/_2$, etc., three-fourths of the molecules

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[34] Dennison, *Proc. Roy. Soc. (London),* **115A,** *483 (1927).*

being in the latter series. For the first series (the only one effective at the lowest temperatures) $n_2^2 - n_1^2 = {}^{25}/_4 - {}^1/_4 = 6$. The second series gives ${}^{49}/_4 - {}^9/_4$ or 10. It would seem that under certain conditions Dennison's mixture would evolve up to 100 cal. per mole when passed over a palladium catalyst. Although the first energy jump is a part of the specific heat curve that must be fitted, we do not imply that it is the only requirement; any theory whatever can be made to give this energy jump by adjusting the moment of inertia.

At 145°K. the rotational heat content is estimated from Fig. 3 to be around 35 cal./mole (by graphical integration), and this is small compared to 1035 cal. Accordingly, since also the amount of gas in the 2nd resonated state is here around 0.01%, Lewis' assumptions are nearly justified at temperatures as high as 150°K. Making allowance for about $3^1/_2$% of the gas not in the lowest state at 145°K. we find an increase in the value of E of 25 cal., so that finally $E = 1060$ cal. and $P = 1.69$. It is possible that these values for E and P may be found a little high (that is, they should be closer to the values 1035 and 1.51, respectively) when allowance is made for the molecules in the second activated state. This will be considered in a subsequent paper.

As this work was made possible by the loan of valuable clocks and condensers by the Departments of Physics and Astronomy, we take this opportunity of expressing hearty appreciation, especially to Professors L. B. Loeb and R. T. Crawford of those Departments. We must acknowledge our indebtedness to Dr. R. M. Buffington for suggestions in connection with calibrating the thermocouples, and to Dr. W. F. Giauque for many of the points in our quantum theory discussion

Summary

A rapid precision method, capable of an accuracy of ${}^1/_{1,000,000}$, is described for measuring the frequency of any regularly oscillating circuit, and the properties of certain "audio-frequency" oscillators are discussed. Details are given of rigorous calculation of the specific heats of hydrogen from the velocity of sound. The thermal expansion of a sample of brass at low temperatures is measured and the hydrogen thermometer is briefly discussed. Details are given of the construction and operation of a thermostat 180 cm. long for low or moderately high temperatures. The claim by Stock and Ritter of large variations in the composition of atmospheric air is shown to be baseless. Measurements of the velocity of sound in hydrogen gas, and the corresponding calculated specific heats, are given for the range 80 to 373°K. The energy difference between the first two rotational states of the hydrogen molecule is shown, by a method of calculation due to G. N. Lewis, to be 1060 cal. per mole, and the relative "probabilities" of the first two states are found to be 1:1.69 (Reiche's best

equation giving 1160 and 1:2, respectively). The effect of a confining tube on the velocity of sound in a gas is found to be accurately given by the formula of Kirchhoff and Helmholtz. Neglect of that fact caused errors of over 10% in the sound velocity specific heat measurements of Partington and Shilling, making their work worthless unless recalculated. The velocity of sound in unconfined, dry, carbon dioxide-free air at 24° is found to be 345.66 meters per second and the velocity of sound in free hydrogen at 0° is found to be 1260.9 meters per second.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

DISPLACEMENT OF METALS FROM SOLUTIONS OF THEIR SALTS BY LESS ELECTROPOSITIVE ELEMENTS

IV. POTASSIUM AMMONO BERYLLATE AND SODIUM AMMONO BERYLLATE

BY F. W. BERGSTROM

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In attempting to prepare aluminum amide by the action of ammonium bromide—an acid in liquid ammonia—upon a solution of sodium ammono aluminate in accordance with the equation, $Al(NH_2)_2NHNa + NH_4Br = NaBr + NH_3 + Al(NH_2)_3$,[1] the author obtained precipitates which varied in composition approximately between the limits of $Al(NH)NH_2$ and $Al_2(NH)_3$. In explanation of this behavior it is suggested that these precipitates be regarded as indefinite compounds resembling the hydrous oxides in constitution, and therefore appropriately called ammonous aluminum nitrides, $AlN + xNH_3$. In view of the chemical similarity between aluminum and beryllium one might expect that beryllium amide would likewise prove to be an ammonous beryllium nitride. The present investigation was then undertaken primarily for the purpose of preparing beryllium amide or an ammonous beryllium nitride. As the potassium ammono beryllate required in the expected reaction, $Be(NHK)_2 + 2NH_4Br = Be(NH_2)_2 + 2NH_3 + 2KBr$, is unknown, the first experiments were directed toward the preparation of this compound.

Potassium Ammono Beryllate.—Since potassium hydroxide dissolves metallic beryllium to form potassium aquo beryllate, we should expect the analogous base of the ammonia system, potassium amide, to dissolve beryllium to form a potassium ammono beryllate. N. C. Jones and P. F. Frohring, at Western Reserve University in the summer of 1926, found that beryllium dissolves in solutions of sodium and potassium amides in liquid ammonia to form extremely soluble ammono beryllates

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[1] Bergstrom, *J. Phys. Chem.*, March, 1928. This reaction resembles the precipitation of aluminum hydroxide by the addition of an acid to a solution of an aquo aluminate in water.

which they were unable to analyze in the time at their disposal. It was for the added purpose of bringing to completion the preliminary work of Jones and Frohring that this portion of the present investigation was undertaken.

Beryllium reacts with potassium amide dissolved in liquid ammonia to form an opaque blue solution, which was shown to contain metallic potassium,[2] the reaction probably proceeding in accordance with the equation, $Be + 2KNH_2$ $Be(NH_2)_2 + 2K$. The apparent anomaly of beryllium replacing the more electropositive element potassium can readily be understood if one recalls the fact that dilute solutions of the alkali metals in liquid ammonia are salt-like in character.[3] The (+) ions in such solutions are the normal ions of the alkali metal, while the (−) ion is the solvated negative electron, e^-. Now beryllium does not dissolve in liquid ammonia to form a solution sufficiently concentrated to exhibit a blue color such as characterizes solutions of the alkali and alkaline earth metals in this solvent. Nevertheless, one may ascribe an extremely slight solubility to beryllium in view of the fact that all of the very electropositive metals, including magnesium, dissolve, at least to some extent, in ammonia. One may assume, by analogy with the alkali metals, that beryllium dissolves to a slight degree in ammonia to form Be^{++} ions together with an equivalent number of solvated negative electrons. Since potassium amide forms K^+ and NH_2^- ions, the reaction of this base with beryllium will simply involve interaction between the ions Be^{++}, NH_2^-, K^+ and e^-. $Be(NH_2)_2$ is very slightly soluble in ammonia and so will form to some extent as a precipitate, leaving in solution equivalent quantities of K^+ and e^- ions, which constitute a solution of metallic potassium. Since $Be(NH_2)_2$ is not entirely insoluble in ammonia it is necessary to consider the above reaction as an equilibrium.

Potassium, formed in the reaction of the preceding paragraph, reacts with the solvent, in the presence of a catalyst such as beryllium, to form potassium amide and hydrogen, while the potassium amide thus formed dissolves the amphoteric base beryllium amide to form potassium ammono beryllate, in the sense of the equation, $Be(NH_2)_2 + KNH_2 = Be(NH_2)\text{-}NHK{\cdot}NH_3$. Aluminum has previously been found to react with potassium amide in an entirely analogous manner.[4]

Potassium ammono beryllate is, however, most conveniently prepared by the action of a solution of metallic potassium in liquid ammonia upon an excess of beryllium. The metallic beryllium, acting as a catalyst, first converts the potassium to potassium amide, which in turn reacts with the beryllium in accordance with the equations of the preceding paragraph.

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[2] Bergstrom, This Journal, 45, 2789 (1923), has described the test used.

[3] Kraus, *ibid.*, 44, 1224 (1922).

[4] Bergstrom, ref. 2, p. 2788; 46, 1548 (1924).

For the purpose, then, of preparing potassium ammono beryllate, a small tube containing about **0.35** g. of potassium is placed in one leg of a reaction tube[5] together with about two atomic equivalents of metallic **beryllium.**[6] Within a day or two after ammonia is distilled into the reaction tube the potassium is completely converted into a colorless solution of potassium ammono beryllate, which is then decanted into the other leg of the reaction tube to effect a separation from the residue of unused beryllium. Attempts to obtain crystals from a concentrated solution of potassium ammono beryllate at −40° having failed, analyses were made of the colorless solid remaining after evaporation of solvent ammonia from the reaction tube.

Potassium ammono beryllate is vigorously hydrolyzed by water to potassium hydroxide, ammonia and beryllium hydroxide, the latter remaining partly in solution as potassium aquo beryllate. In preparation for analysis the products of the hydrolysis were dissolved in dilute sulfuric or hydrochloric acid. Beryllium was determined on an aliquot portion of this solution as oxide, according to the method of Bleyer and Boshart.[7] Potassium was recovered as sulfate or chloride from the filtrate of the beryllium hydroxide. Nitrogen in a second aliquot portion was estimated volumetrically as ammonia.

Preparation 1, dried in a vacuum at 20°, weighed **0.8776** g. At 185° in a vacuum it lost **0.1071** g. of ammonia of crystallization. (The ammonia was not all pumped off.) One-fourth of the preparation gave **0.0736** g. of nitrogen. Another fourth gave **0.0582** g. of BeO and **0.1696** g. of KCl.

Preparation 2, dried in a vacuum at 20°, weighed **0.8478** g. Heated in a vacuum at 160° it lost **0.1388** g. of ammonia. One-fourth gave **0.0623** g. of nitrogen. A second fourth gave **0.0560** g. of BeO and **0.1674** g. of KCl.

Preparation 3, dried in a vacuum at −40°, weighed **0.8244** g. In a vacuum at 25° it lost **0.0067** g. and at 215° a further **0.1382** g. of ammonia. One-half gave 0.1080 g. of BeO. One-quarter gave **0.1584** g. of KCl. One-quarter gave **0.0603** g. of nitrogen.

Analyses.—Calcd. for $Be(NH_2)NHK{\cdot}NH_3$: Be, **9.4;** N, **43.7; K, 40.7.** Found, dried in a vacuum at room temperature: Be, **9.6, 9.5, 9.5; N, 43.6, 42.9, 43.4; K, 40.6, 41.4, 40.7.** This salt, when converted into $Be(NH_2)NHK$, should lose **17.7% of** ammonia. Specimens No. **2** and **3** lost, respectively, **16.4** and **17.6%** of ammonia when heated in a vacuum above **160°.**

Potassium ammono beryllate may be represented as a salt of the ammonia system, $Be(NH_2)NHK{\cdot}NH_3$, as a double compound of beryllium amide and potassium amide, $Be(NH_2)_2{\cdot}KNH_2$, or, following Werner, as the coordination compound, $K[Be(NH_2)_3]$. In accordance with the

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[5] A description of the manipulations concerned in the preparation of compounds in liquid ammonia may be found in the following articles by Franklin and his students: THIS JOURNAL, 27, **832 (1905);** 29, **1694 (1907);** 35, **1460 (1913);** J. Phys. *Chem.,* 15, **510 (1911);** 16, 694 **(1912).**

[6] The beryllium, which was in the form of small chips, was found to **be** practically free from other metals.

[7] Bleyer and Boshart, *Z.* anal. *Chem.,* **51, 754 (1912).**

fact that beryllium resembles aluminum more closely in properties than it does magnesium, potassium ammono beryllate was found to resemble potassium ammono aluminate, $Al(NH_2)_3 \cdot KNH_2$, more closely in constitution and properties than it does potassium ammono magnesiate, $Mg(NH_2)_2 \cdot 2KNH_2$.[8] Both potassium ammono aluminate and potassium ammono beryllate are readily soluble in liquid ammonia and both melt in their ammonia of crystallization upon heating, each losing one molecule of ammonia. Potassium ammono magnesiate, on the other hand, is very slightly soluble in ammonia and does not readily lose ammonia when heated.

Sodium **Ammono** Beryllate.—This salt is best prepared in the same manner as potassium ammono beryllate, that is, by the action of a liquid ammonia solution of sodium upon an excess of metallic beryllium.

Preparation 1, dried in a vacuum at 20°, weighed 1.2017 g. One-quarter gave 0.0950 g. of BeO and 0.2743 g. of Na_2SO_4. One-quarter gave 0.1537 g. of nitrogen.

Preparation 2, dried in a vacuum at 20°, weighed 1.0378 g. One-half gave 0 2696 g. of nitrogen. The other half gave 0.1646 g. of BeO and 0.3847 g. of NaCl.

Preparation 3, dried in a vacuum at −40°, weighed 0.8035 g. When heated in a vacuum at room temperature, 0.0038 g. of ammonia of crystallization was lost. One-quarter gave 0.1032 g. of nitrogen. Another quarter gave 0.0633 g. of BeO and 0.1497 g. of NaCl.

Analyses.—Calculated for $Be(NH_2)NHNa \cdot NH_3$: Be, 11.2; N, 52.5; Na, 28.8. Found, dried in a vacuum at room temperature: Be, 11.4, 11.4, 11.4; N, 51.2, 52.0, 51.6; Na, 29.6, 29.2, 29.5. These analyses indicate that sodium ammono beryllate has lost a little of its ammonia of crystallization in a vacuum at room temperature. When heated in a vacuum between 150 and 200°, sodium ammono beryllate melts and loses approximately one molecule of ammonia.

Sodium ammono beryllate resembles the corresponding potassium salt closely in physical and chemical properties.

Beryllium Amide.—It was hoped that beryllium amide would be formed, in accordance with the equation, $BeI_2 + 2KNH_2 = 2KI + Be(NH_2)_2$, when potassium amide is added to a solution of a salt of beryllium in liquid ammonia. Unfortunately, potassium amide precipitates ammonobasic mixtures from solutions of both beryllium iodide and thiocyanate.

When a solution of ammonium bromide is slowly poured into a solution of sodium ammono beryllate, a flocculent, white precipitate containing much sodium is thrown down instead of the expected beryllium amide.

Magnesium amide may be formed by the action of a liquid ammonia solution of sodium chloride or iodide upon magnesium.[9] An attempt to prepare beryllium amide by the analogous action of a solution of sodium chloride on beryllium failed.[10]

[8] Franklin, THIS JOURNAL, 35,1463 (1913).

[9] Bergstrom, *ibid.*, 48,2849 (1926).

[10] Since beryllium chloride is very soluble in liquid ammonia at room temperature, there is no tendency for the reaction $Be + 2NaCl \qquad BeCl_2 + 2Na$ to take place.

Notes.—Since a solution of sodium ammono magnesiate attacks magnesium to form magnesium amide,[9] it was expected that a solution of sodium ammono beryllate would likewise react with magnesium to form magnesium amide. The anticipated reaction does not take place. Magnesium amalgam, however, reacts with a solution of sodium ammono beryllate to form a very impure magnesium amide and sodium amalgam.

Addition of a solution of sodium ammono beryllate to a solution of magnesium thiocyanate throws down a flocculent precipitate of the composition $Mg(NH_2)_2 \cdot Be(NH_2)_2$, which may be a mixture of beryllium and magnesium amides and not a definite compound.

A solution of sulfur in liquid ammonia reacts slowly with beryllium to form a yellow precipitate of an ammonated beryllium mono- or polysulfide. This precipitate slowly dissolves in an excess of sulfur solution to form soluble polysulfides of beryllium.

Beryllium, the surface of which has been cleansed by the action of a liquid ammonia solution of ammonium chloride,[11] does not dissolve in pure liquid ammonia to form a visibly colored solution. Under similar conditions it will be remembered that magnesium dissolves to form a light blue solution.[12]

In conclusion, the author wishes to express his thanks to Dr. E. C. Franklin for his interest in this work and for reading the manuscript prior to publication.

Summary

(1) Potassium and sodium ammono beryllates of the general formulas $Be(NH_2)NHK \cdot NH_3$ and $Be(NH_2)NHK$ have been prepared by the action of solutions of the corresponding alkali metal or alkali metal amide upon metallic beryllium.

(2) Attempts to prepare beryllium amide, $Be(NH_2)_2$, have failed.

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[11] Ammonium chloride is an acid in liquid ammonia. Franklin and Kraus, Am. Chem. J., 23, 305 (1900); THIS JOURNAL, 27, 822 (1905).

[12] Cottrell, J. *Phys. Chem.*, 18, 96 (1914).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

THE ACTION OF LIQUID AMMONIA SOLUTIONS OF AMMONIUM SALTS ON METALLIC BERYLLIUM. AMMONATED BERYLLIUM HALIDES AND AMMONOBASIC BERYLLIUM SALTS

BY F. W. BERGSTROM

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Franklin and Kraus[1] have pointed out that many substances, among which are the hydrogen halides, are acids in liquid ammonia solution as well as in water. It has indeed been shown that solutions of these acids in liquid ammonia, in the form of course of their ammonium salts, react with most elements more electropositive than nickel.[2] One should then expect the electropositive element beryllium to react readily with solutions of ammonium salts in liquid ammonia. Since aqueous solutions of the normal salts of beryllium dissolve this metal to form very soluble aquo basic salts, it should be possible to prepare a series of ammonobasic beryllium salts by the action of solutions of the normal salts in liquid ammonia upon an excess of beryllium. Bearing in mind the difficulties encountered in crystallizing basic beryllium salts from water,[3] it became of added interest to attempt their preparation in liquid ammonia in the hope of obtaining crystallizable compounds. As a secondary purpose of this investigation it was hoped to prepare beryllium amide by the action of potassium amide upon a soluble beryllium salt, in the sense of the equation $BeI_2 + 2KNH_2 = Be(NH_2)_2 + 2KI$.

Newton C. Jones,[4] working under Dr. Franklin at Western Reserve University in the summer of 1926, found that beryllium dissolves readily in liquid ammonia solutions of an excess of ammonium chloride, ammonium ammono nitrate (ammonium azide), ammonium thiocyanate, ammonium iodide and ammonium cyanide with the evolution of hydrogen. From the solutions so prepared Jones was in most cases able to crystallize the corresponding normal salts of beryllium with ammonia of crystallization, but he was unable definitely to determine their composition in the limited time at his disposal.

Beryllium Chloride Diammonate and Tetrammonate, $BeCl_2 \cdot 2NH_3$ and $BeCl_2 \cdot 4NH_3$.—Normal beryllium chloride may readily be prepared by dissolving beryllium in a solution of more than two equivalents of ammonium chloride in liquid ammonia. From this solution, cooled to $-40°$,

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[1] Franklin and Kraus, *Am. Chem. J.*, 23, 305 (1900); THIS JOURNAL, 27, 822 (1905).

[2] Bergstrom, *J. Phys. Chem.*, 29, 160 (1925).

[3] Parsons, "The Chemistry and Literature of Beryllium," The Chemical Publishing Co., Easton, Pa., 1909, pp. 61–71, where references are given to the literature prior to 1909.

[4] Unpublished work.

there separates an abundant crop of well formed, colorless crystals which, after drying in a vacuum at $-40°$ or at room temperature, correspond in composition to the formula $BeCl_2 \cdot 4NH_3$. When heated in a vacuum at 210–255°, two molecules of ammonia of crystallization are lost and $BeCl_2 \cdot 2NH_3$ is formed.

Unlike most metallic chlorides, beryllium chloride is readily soluble in liquid ammonia at room temperature. Solutions of beryllium chloride of proper concentrations separate into two liquid phases which have a lower consolute temperature between 0 and $-40°$. Other compounds have been found which exhibit a similar behavior in liquid ammonia.[5]

A description of a typical preparation of beryllium chloride will serve to illustrate the general method by which all of the normal and ammonobasic halides of beryllium were made.

In one leg of a two-legged liquid ammonia reaction tube[6] was placed 0.10 g. of metallic beryllium[7] together with 0.63 g. or 2.5 equivalents of ammonium chloride. Ammonia was distilled into the tube to dissolve the ammonium chloride, after which the apparatus was set aside for a few hours until all of the beryllium had gone into solution. To effect separation from a small quantity of insoluble material, the clear solution of beryllium chloride was decanted into the other leg of the ,reaction tube. By cooling this solution in a bath of liquid ammonia there was obtained a good crop of colorless crystals. After one recrystallization, the salt was dried in a vacuum at 20 and 210°, hydrolyzed by water and dissolved in dilute sulfuric acid. Beryllium in an aliquot portion of this solution was determined as oxide after a previous precipitation as hydroxide according to the method of Bleyer and Boshart.[8] On other aliquot portions, chlorine was determined as silver chloride and nitrogen was estimated volumetrically as ammonia.

Anal. Calcd. for $BeCl_2 \cdot 4NH_3$: Be, 6.1; N, 37.8; Cl, 47.9. Found, dried in a vacuum at 20°: Be, 6.2, 6.5; N, 37.9, 37.8; Cl, 47.8, 47.7. When these specimens were heated in a vacuum at 210 and 255°, they lost, respectively, 22.0 and 23.0% of ammonia; calculated for the loss of two molecules of ammonia from the tetrammonate, 23.0%. Beryllium chloride retains only four molecules of ammonia in a vacuum at $-40°$.

Beryllium Bromide Tetrammonate, $BeBr_2 \cdot 4NH_3$.—Beryllium bromide is readily obtained by dissolving beryllium in an excess of a liquid ammonia solution of ammonium bromide. Following the preliminary work

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[5] Bergstrom, J. *Phys. Chem.*, 29, 162 (1925); THIS JOURNAL, 46, 1559 (1924).

[6] For more complete descriptions of the manipulations necessary for the preparation of compounds in liquid ammonia and their subsequent analysis, see Franklin and co-workers, (a) THIS JOURNAL, 27,831 (1905); (b) 29, 1694 (1907); (c) 35,1460 (1913); (d) J. *Phys. Chem.*, 15,510 (1911); (e) 16,694 (1912).

[7] The beryllium, which was in the form of small chips, was found to be practically free from other metals.

[8] Bleyer and Boshart, Z. anal. *Chem.*, *51*, 754 (1912).

of Jones,[4] it was expected that an ammonated beryllium bromide would crystallize from solutions at low temperature, but for some reason protracted cooling of a concentrated solution of this specimen at −40° failed to cause the formation of crystals. The reaction tube was then set aside for a week to allow a gradual concentration of the solution by leakage of ammonia past a defective stopcock. The well formed crystals of beryllium bromide thus obtained were washed with a small quantity of solvent, dried in a vacuum at 20° and analyzed.

Anal. Calcd. for $BeBr_2 \cdot 4NH_3$: Be, 3.8; N, 23.6; Br, 67.4. Found: Be, 3.7; N, 24.2; Br. 67.4.

Biltz and Messerknecht[9] have prepared beryllium chloride with 2, 4, 6 and 12 molecules, and beryllium bromide with 4, 6 and 10 molecules, of ammonia of crystallization.

Ammonobasic Beryllium Chloride.—A solution of ammonium chloride in liquid ammonia dissolves metallic beryllium to form normal beryllium chloride, and this in turn reacts with an excess of the metal to form a colorless, very slightly soluble ammonobasic beryllium chloride. One preparation was found on analysis to be a little more basic than indicated by the formula, $BeCl_2 \cdot Be(NH_2)_2 \cdot xNH_3$. However, one of Dr. E. C. Franklin's students at Western Reserve University reports a number of preliminary analyses agreeing more closely with this formula. Perhaps this is not a definite compound, for the basic halides of the composition $Be(NH_2)_2 \cdot BeBr_2$ and $Be(NH_2)_2 \cdot BeI_2$ have not been obtained.

Ammonobasic Beryllium Bromides: $2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$, $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$ and $3Be(NH_2)_2 \cdot BeBr_2 \cdot 8NH_3$. Experiment 1.—A liquid ammonia solution of 0.69 g. of ammonium bromide was poured upon 0.06 g., or one atomic proportion, of beryllium in one leg of a reaction tube. There resulted a rather brisk evolution of hydrogen. Upon examining the reaction tube the next morning, it was found that the beryllium had disappeared, being in part replaced by a number of small white crystals of an ammonobasic beryllium bromide. The solution in equilibrium with this precipitate consisted of two liquid phases which had a lower consolute temperature between 10 and 15°. The crystals were washed to free them from material soluble in liquid ammonia. After evaporation of solvent from the reaction tube, the two legs were separated before the blast lamp and their respective contents submitted to analysis.[10]

Excepting that larger quantities of ammonium bromide and beryllium were used, the subsequent experiments were essentially duplicates of the first. In Experiment 3 the sparingly soluble crystals alone were analyzed.

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[9] Biltz and Messerknecht, *Z. anorg. Chem.*, 148,157 (1925).

[10] The crystals were sealed off in the leg of the reaction tube to which the stopcock was attached. The leg containing the washings of the crystals was drawn down in the blast flame and a small stopcock tied on with rubber tubing.

TABLE I

ANALYSES OF THE SPARINGLY SOLUBLE AMMONOBASIC BROMIDE

	Calcd. for $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$	Found, dried in a vacuum at 20° 1	2	3	4
Be	10.0	10.5	10.4	10.4	10.3
N	38.9	38.8	38.8	38.7	38.6
Br	44.4	45.2	44.4	44.5	44.3

When dried in a vacuum at −40°, specimen No. 3 corresponded in composition to $3Be(NH_2)_2 \cdot BeBr_2 \cdot 8NH_3$. Calcd.: Be, 8.4; N, 45.8; Br, 37.4. Found: Be, 8.8; N, 45.3; Rr, *37.7*.

TABLE II

ANALYSES OF THE SOLUBLE AMMONOBASIC BROMIDE

	Calcd. for $2BeBr_2 \cdot Be(NH_2)_2 \cdot 8NH_3$	Found, dried in *a* vacuum at 20° 1	2	4
Be	5.2	5.3	5.4	5.2
N	27.2	27.8	27.4	27.6
Br	62.0	61.2	61.8	61.5

The low bromine and high nitrogen analyses are due in part to the presence in solution of a small quantity of the salt, $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$. There is perhaps some doubt as to the chemical individuality of a substance which could not even be crystallized from solution at −78°, and therefore was analyzed without purification. In support of the view that this salt is a definite compound, it was found that the composition of the soluble material in equilibrium with the crystals of $3Be(NH_2)_2 \cdot BeBr_2 \cdot 4NH_3$ did not change over a period of two weeks. Thus, in the three experiments 1, 2 and 4 the solution was in contact with the crystals of the sparingly soluble basic bromide for 3, 8 and 12 days, respectively.

Ammonobasic Beryllium Iodides (1), $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$.—A solution of ammonium iodide in liquid ammonia reacts rapidly with an excess of beryllium to form the normal iodide and then very soluble ammonobasic iodides. One of these, $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$, can easily be separated in definite crystalline form by cooling a solution of one to two atomic proportions of beryllium in one molecular proportion of ammonium iodide to −40° in a bath of liquid ammonia.

The two preparations, analyses of which are given below, were crystallized in good yield from solutions prepared by the action of ammonium iodide upon one atomic proportion of beryllium.[11] The salt which separated from solution on cooling was again crystallized, dried in a vacuum at 20°, dissolved in dilute sulfuric acid and analyzed. Found: Be, 8.2, 8.1; N, 30.7, 30.6; I, 55.4, 55.8. Calcd. for $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$; Be, 7.9; N, 30.8; I, 55.9. This salt lost very little ammonia when heated in a vacuum at 130°, but lost approximately one molecule when heated to 205°.

(2), $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$.—If a liquid ammonia solution of $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$ is brought in contact with metallic beryllium, the

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[11] In view of this it seems very doubtful whether a salt of the formula $Be(NH_2)_2 \cdot BeI_2 \cdot xNH_3$ exists.

latter slowly dissolves and within the course of a few weeks a point is reached at which an amorphous, white precipitate begins to form. The liquid ammonia solution, separated at this stage by decantation from the unused beryllium and the white precipitate, can be concentrated to an almost unpourable sirup at 20° without crystallization. An analysis of the crude, white solid remaining after evaporation of the solvent ammonia from the reaction tube gave 9.8% Be, 35.4% N and 48.9% I, corresponding roughly to a compound of the formula $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$, which requires 10.1% Be, 36.6% N and 47.3% I.

In an attempt to prepare this compound in a purer condition, the foregoing experiment was repeated. When a moderately concentrated solution of the salt was cooled for some time in an ether-carbon dioxide snow mixture, an abundant crop of small, colorless crystals was obtained. These were freed from mother liquor, dried in a vacuum at 20°, hydrolyzed with water,[12] dissolved in dilute sulfuric acid and analyzed. There was found 10.3% Be, 37.2% N and 47.1% I, in better concordance with the calculated composition of $5Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$ given in the preceding paragraph.

Potassium amide throws down from a solution of the basic salt, $3Be(NH_2)_2 \cdot BeI_2 \cdot 4NH_3$, a flocculent, white precipitate, which was shown by analysis to be an ammonobasic mixture containing approximately ten atoms of beryllium per atom of iodine. In one experiment the solution in equilibrium with this precipitate was found to contain three atoms of beryllium for each atom of iodine,[13] indicating the dissolved substance to be $5Be(NH_2)_2 \cdot BeI_2 \cdot xNH_3$.

Ammonobasic Beryllium Cyanide.—A solution of mercuric cyanide in liquid ammonia reacts with beryllium, as it does with aluminum,[14] to form a double beryllium-mercuric cyanide, and then a very soluble normal beryllium cyanide, which was not isolated in a state of purity because of the ready formation of soluble ammonobasic cyanides by further reaction with beryllium.

Discussion

It is well known that solutions of the normal beryllium salts in water can dissolve large quantities of beryllium hydroxide, extending in the case of the acetate to six equivalents, while the chloride can hold four and the sulfate three.[3,15] On diluting these solutions with water, precipitates of

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[12] This salt is hydrolyzed by water with evolution of heat to form ammonia, ammonium iodide, beryllium hydroxide and possibly aquo basic salts of beryllium.

[13] That is, per atom of iodine not present in the solution as potassium iodide. The latter salt is also a product of the reaction, as the following equation shows: $3[3Be(NH_2)_2 \cdot BeI_2] + 2KNH_2 = 2[5Be(NH_2)_2 \cdot BeI_2] + 2KI$.

[14] Bergstrom, THIS JOURNAL, 46, 1559 (1924).

[15] Sidgwick and Lewis, *J. Chem. Soc.*, 129, 1287–1302 (1926).

a highly basic nature are thrown down, while on evaporation gummy, non-crystalline masses are obtained. Perhaps the only basic beryllium compounds which have been prepared in a state of purity are the salts of the type of basic beryllium acetate, $3Be(CH_3COO)_2{\cdot}BeO$ or $Be_4O(CH_3COO)_6$.[16] In contrast with the difficulty of obtaining aquo basic salts of beryllium in a state of purity from water is the relative ease with which many crystalline ammonobasic halides of beryllium can be prepared in liquid ammonia. It is noteworthy though unexpected fact that the very basic compound, $5Be(NH_2)_2{\cdot}BeI_2$, is much more soluble in liquid ammonia at $-40°$ than the less basic $3Be(NH_2)_2{\cdot}BeI_2$.

In conclusion, the author wishes to thank Dr. E. C. Franklin for his interest in this work and for looking over the manuscript prior to publication.

Summary

I. Beryllium dissolves in liquid ammonia solutions of an excess of ammonium chloride and bromide to form normal beryllium halides with ammonia of crystallization. The salts, $BeCl_2{\cdot}4NH_3$, $BeCl_2{\cdot}2NH_3$ and $BeBr_2{\cdot}4NH_3$ have been prepared.

2. Solutions of the normal halides of beryllium in liquid ammonia readily react with metallic beryllium to form ammonobasic halides; $3Be(NH_2)_2{\cdot}BeBr_2{\cdot}4NH_3$, $3Be(NH_2)_2{\cdot}BeBr_2{\cdot}8NH_3$, $3Be(NH_2)_2{\cdot}BeI_2{\cdot}4NH_3$ and $5Be(NH_2)_2{\cdot}BeI_2{\cdot}4NH_3$ have been prepared in crystalline form. There is good evidence for the existence of $2BeBr_2{\cdot}Be(NH_2)_2{\cdot}8NH_3$, although it has not been obtained in crystalline form.

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

THE SOLUBILITY OF SILVER IN MERCURY[1]

BY ARTHUR A. SUNIER AND C. B. HESS

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In connection with work on solutions in this Laboratory, attention was directed to the lack of conclusive data on the solubility of silver in mercury. Many determinations have been made at isolated temperatures[2] but, to our knowledge, Joyner[3] has made the only systematic attempt to investigate this system over a range of temperatures. Yet his work,

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[16] Parsons, ref. 3, pp. 62–64; Bragg and Morgan, Proc. Roy. *Soc.* (London), **104A,** 437 (1923); Morgan and Astbury, ibid., **112A,** 441 (1926).

[1] This paper was presented by one of the authors (C. B. H.) at the 1927 Spring Meeting of the American Chemical Society, held in Richmond, Virginia.

[2] (a) Gouy, J. *phys.,* [3] 4, 320 (1895); (b) Humphreys, J. *Chem. Soc.,* 69, 243 (1896); (c) Reinders, *Z. physik. Chem.,* 27, 285 (1898); (d) Ogg, *ibid.,* 50, 209 (1905); (e) Eastman and Hildebrand, THIS JOURNAL, 36, 2020 (1914).

[3] Joyner, J. *Chem. Soc.,* 99, 195 (1911).

dealing mainly with the ternary system tin-silver–mercury is not accompanied by sufficient control work to weight his results properly on silver and mercury alone.

The present paper is a report of solubility determinations of silver in mercury up to 200°.

Materials

The mercury used was first washed by dropping it five times through a five foot Meyer column containing mercurous nitrate. The dried mercury was then distilled three times from an all-glass apparatus according to the method of Hulett and Minchin.[4] Samples of the purified product yielded no residue when carefully distilled in *vacuo*.

Two samples of silver were used. The first, employed in what are later to be described as Series A, B, C determinations, was U. S. Mint bar of the "999" fineness. Filings of this were obtained with a clean, hard file. Because traces of iron were appearing in the final analyses, a second sample was used in our final (Series D) determinations. This was 1000 fine foil, very kindly supplied us by the Philadelphia Mint. Thin strips of this were used in charging the solubility tubes. Below (Table I) are given the results of analysis of both samples by the authors.

Table I

Analysis of Silver Used

					Av.
Ag filings, % Ag	99.76	99.72	99.71	99.73	99.73
Ag foil, % Ag .	99.97	99.96	99.96	99.96	99.96

Apparatus

The solubility tube (Fig. 1) was made of Pyrex glass. It consists essentially of a sample tube B with projections C for suspending it in the balance case, a capillary filter finely constricted at D, a glass-wool filter E and a lower tube F in which the amalgams were prepared.

For stirring the amalgams a long, vertical rod pivoted at its center was used. The lower end of this rod had two projecting posts so spaced that the two eyes of the tubes could be slipped over them. The upper end of the rod was slotted and attached to the arm of an automobile windshield cleaner. When in operation a pendulum-like motion was imparted to the solubility tubes on the lower end of the rod of such an amplitude as to completely transfer the amalgams from one end of the tubes to the other.

The thermostat, a ten-gallon copper tank heavily lagged, contained cylinder oil which had a flash point of 275°. After three months' use this oil did not smoke appreciably at 180° and showed no evidences of carbonization or lowering of the flash point. Four double paddle stirrers

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[4] **Hulett** and Minchin, *Phys. Rev.*, **21, 388 (1905).**

(1000 r.p.m.) kept the oil in violent agitation. Heat was supplied by four 500-watt immersion heaters. Thermal balance at any temperature was obtained by the use of two circular nichrome heating elements of variable resistance immersed in the bath near the top and bottom. The mercury thermo-regulator operated a 40-watt elongated bulb. Beckmann thermometers permanently placed in the bath showed a deviation of much less than 0.1° over a period of eight hours.

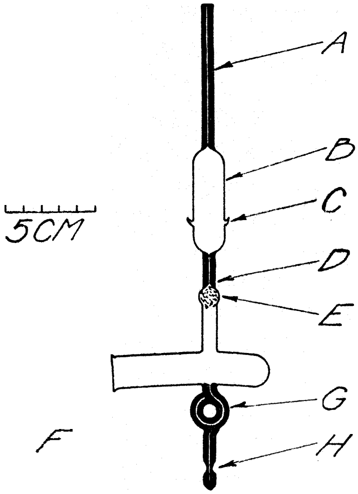

Fig. 1.

Temperatures were read from a mercury thermometer especially standardized for this investigation by the Physical Laboratory of the Taylor Instrument Companies. At the conclusion of the solubility work, this thermometer was compared against one recently standardized for us by the Bureau of Standards.

The amalgam samples were vacuum distilled from an all-glass apparatus previous to analysis. A Cenco pump produced a vacuum of 0.003 mm. Pressures were read from a McLeod gage capable of being read to 0.001 mm.

Experimental Procedure

About 7 cc. of pure mercury and excess silver were put into the Tube F (Fig. 1), which was then sealed off. Capillary A was connected to a Cenco pump and the amalgam boiled out, when the tube was sealed off from the pump and A bent into an eye. A fine wire was attached at G and the constricted capillary H file marked, The eyes on the tubes enabled them to be slipped onto the stirrer posts, the whole device then being firmly clamped in the thermostat.

For a determination of the solubility at a certain temperature, saturation in every case was attained from the low and then from the high temperature side. In the former case the shaker with four tubes was started and the bath raised to the desired temperature, which usually required about an hour. After thermal balance was established at this temperature, the tubes were shaken for an additional period of three hours and then sampled.

For the corresponding high side determination, four tubes were inserted in the hot-bath, the temperature was raised about 20°, held there for an hour or more and then allowed to drop back to the determination temperature. This preheating, occupying from three to five hours, was succeeded by the usual three hour shaking at constant temperature and sampling.

The remarkable agreement between these two measurements at every temperature was sufficient evidence that equilibrium was being attained.

When the amalgams were ready to be sampled, the shaker was stopped and a tube slipped off, keeping it at all times below the oil surface. The counterweighted eye A was then released and the wire on G firmly held, when the tube inverted under the oil Carefully drawing up the wire until the tip H just protruded (Fig. 2), the exposed capillary was wiped dry and broken under clean rubber tubing. Atmospheric pressure forced the amalgam through the glass wool filter E into the lower tube. After filtration the tubes were removed from the bath, dried and cooled. Sample tube B was cut off, suspended in the balance case and weighed. The amalgam samples were then transferred to the distillation tubes and boiled out prior to distillation. All glassware with which the cooled amalgam came in contact was treated later in the analysis with nitric acid.

The tubes containing the amalgams were sealed to the distillation apparatus and the system was evacuated. The temperature was gradually raised to about 200°, distillation requiring about two hours. The residues were then flamed in the vacuum to the softening point of Pyrex. Separate control distillations established the fact that these residues consisted approximately of 1 atom of mercury to 50 of silver.

Tubes and contents were then transferred to beakers and treated with 10 cc. of concentrated nitric acid. After boiling, the solutions were diluted, the tubes removed and the silver was precipitated with dilute hydrochloric acid. Digestion until the volumes were well below 50 cc. was followed by filtration, re-solution of the silver chloride with ammonia, and a second precipitation and digestion to small volume. Porcelain crucibles with unglazed porous bottoms were used in the weighing.

Before adopting the above method of analysis, much control work was done on the methods available. The first investigated was that of Joyner,[3] devised to provide for the appreciable solubility of silver chloride in mercuric nitrate solutions.[5] The standard blowpipe method was also studied, using cupels of dental investment compound. In Table II are given results using each method for the analysis of 400 mg. of silver dissolved in 5 cc. of mercury. In Joyner's method the amalgam is dissolved directly in nitric acid; in the other two, distillation was first carried out.

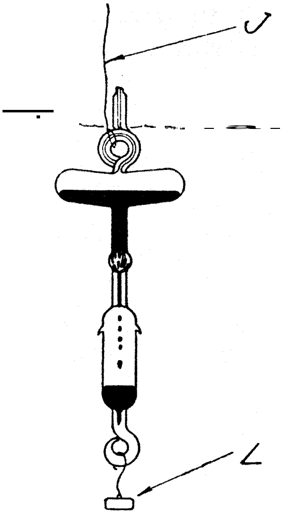

Fig. 2.

TABLE II

COMPARISON OF ANALYTICAL METHODS

Method	Joyner	Blowpipe	Present paper
% Ag recovered	99.38	98.8	99.78
	99.03	99.4	99.66
	98.45	99.9	99.78
	98.94	..	99.69
Av.	98.95	99.0	99.73

To test the whole experimental arrangement, four tubes were made up containing weighed amounts of silver and mercury and carried through the entire procedure outlined above, including shaking in the bath for three hours and sampling; in Table III are given the results.

TABLE III

ANALYSIS OF AMALGAMS OF KNOWN CONCENTRATION

Atomic % of silver taken	0.847	0.869	0.854	0.697
Atomic % of silver found	0 845	0.867	0.851	0.694

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[5] Buttle and Hewitt, *J. Chem. Soc.*, 93,1405 (1908).

Results

In all four series of determinations were made. The first two (**A** and B) were distinctly preliminary and included much of the control work given above. The results were of the same order of magnitude as our final values, except that in the measurements from the high temperature side the method of stirring then in use was not producing equilibrium. The shaking device above described was then installed.

TABLE IV

SOLUBILITY OF SILVER IN MERCURY

(Complete Data for Two Temperatures)

Detn.		Temp., °C	Ag at start g	Wt of amalgam, g.	Wt of AgCl, g.	Atomic % sol.
17-D			0.6	94.128	0.1962	0.291
18-D	Low Side	80.2	6	90.009	.1838	.285
19-D			.6	79.541	.1623	.285
20-D			.6	97.826	.1993	.285
21-D			.5	85.310	,1730	.283
22-D	High Side	80.2	.5	99.137	.2018	.285
24-D			.5	97.910	.2000	.285
					Av.	.286
13-D			.6	93.414	.2760	.413
14-D	Low Side	98.2	.6	84.176	.2494	.414
15-D			.6	67.723	.1985	.409
16-D			.6	93.020	.2737	.411
10-D			.6	97.158	,2840	.408
11-D	High Side	98.2	.6	100.827	.2953	.408
12-D			.6	96.770	.2846	.411
					Av.	.411

TABLE V

SOLUBILITY OF SILVER IN MERCURY

(Summary of Experimental Data)

No. of detns.	Temp., °C.	Atomic % sol.	Av. dev. from mean (p.p.t.)
17–22, 24 D	80.2	0.286	3.5
10–16 D	98.2	.411	4.9
10–12, 14–17 C	121.9	.612	1.6
15–19, 21 C	144.5	.849	1.2
1, 3, 4, 6–8 D	160.6	1.057	7.6
25–27, 29–32 D	177.9	1.346[a]	2.2
34–40 D	198.9	1.746[a]	5.2

[a] At these higher temperatures it was feared that the large precipitate of AgCl obtained in the analysis might have contained mother liquor or salt in the precipitation from the small volumes necessary in working at the lower temperatures. Mr. G. H. Reed, working in this Laboratory, repeated the measurements above 180" using greater care in the washing and drying of the AgCl. His results were about 0.03 atomic per cent. lower than ours. They are

Temp., °C.	181.8	193.3	212.7
Solubility, atomic %	1.365	1.573	1.953

TABLE VI

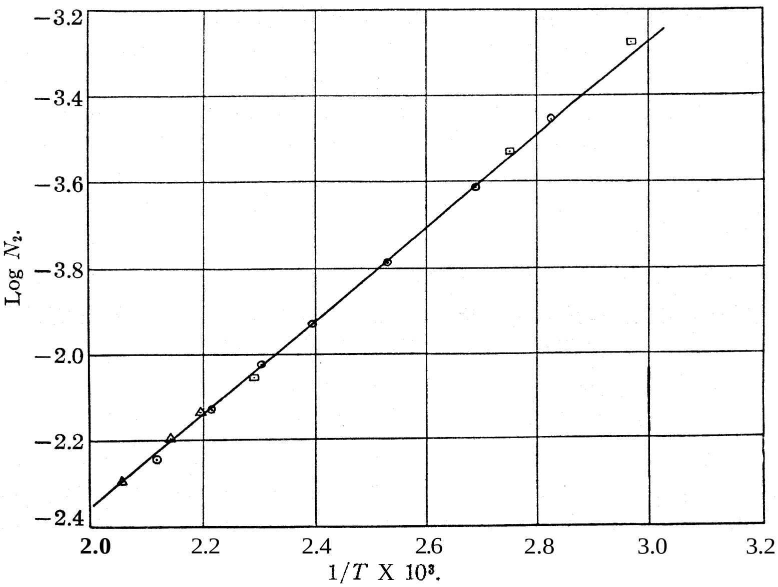
SOLUBILITY OF SILVER IN MERCURY AT ROUNDED TEMPERATURES

(From Log N vs. $1/T$ Plot)

Temp, °C.	100 N (from curve)	100 N (calcd.)	Error, p.p.t.
80.0	0.288	0.286	7
100.0	.419	.419	0
120.0	587	.587	0
140.0	.797	.797	0
160 0	1 053	1.050	3
180.0	1 356	1.350	4
200.0	1 708	1 700	4

Of the 56 final determinations only eight have been omitted. Of these six were due to poor filtering, oil in tubes, or bumping in distillation. Two determinations only were rejected because their deviation from the mean was more than 4 times the average deviation for that temperature.

All solubilities are given in atomic per cent. (atoms of silver per 100 total atoms).



□, Joyner; △, Reed, ⊙, Authors.

Fig. 3.—Solubility of silver in mercury.

Discussion of Results

In Fig. 3 the results are plotted as log N vs. $1/T$. The values of Joyner and Reed have been distinguished from those of the present authors. Very satisfactory agreement is found in the various results.

This agreement is particularly of interest since Joyner used thermostatting periods of a fortnight in the preparation of his amalgams. He also used a pipet for sampling, an instrument which in the hands of others has often led to fictitious solubility data.

Joyner's data show, in some cases, an experimental error of 200 p.p.t. Much of this is undoubtedly due to his method of sampling.

A large scale plot was carefully constructed and used in determining the equation for the straight line which results. The equation which has been found to hold satisfactorily is $\log_{10} N = -1074.2(1/T) + 0.501$. The rounded solubility values in Table VI were obtained from this large plot. The calculated values in Table VI are those obtained using the above equation; the agreement is seen to be quite satisfactory.

In the analysis of the amalgams, it was found that distillation at 0.1 mm. and 200° yielded a residue of the approximate composition Ag_3Hg_4. As has been mentioned above, increasing the vacuum to 0.003 mm. and using flame temperatures, a residue composed of about 1 atom of Hg to 50 of Ag was obtained. There is every reason to believe that with a further decrease in pressure in distillation, results found by weighing the residues as silver would be fully as accurate as most wet methods for the determination of silver in the presence of mercury.

The authors wish to thank Professor Willard R. Line of the University of Rochester for his help in the analytical phase of the work.

Summary

1. A method of preparing and analyzing silver amalgams has been described which yields results uniformly only 2 p.p.t. low.

2. A tube has been developed of general applicability to solubility work, which permits of sampling without removal of the equilibrium mixture from the thermostat or the introduction of sampling devices.

3. This tube has been used to determine the solubility of silver in mercury up to 200°, over fifty determinations having been made.

ROCHESTER, NEW YORK

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

THE ADSORPTION OF ORGANIC COMPOUNDS ON HYDROUS OXIDES AND FULLER'S EARTH

BY DONALD P. GRETTIE WITH ROGER J. WILLIAMS

RECEIVED OCTOBER 13, 1927 PUBLISHED MARCH 7, 1928

Adsorbents have not infrequently been used in the separation of materials of biological importance from extracts of tissues containing them. They have been used in this Laboratory for work of this nature where attempts are being made to isolate a "bios" from yeast extracts. The desire to use adsorbents as intelligently as possible made it desirable to have data on the adsorption of various organic compounds by different adsorbents under comparable conditions. The particular question which appeared most interesting to us was whether the adsorption of various compounds would take place in accordance with the acidic and basic properties of the adsorbent and adsorbate, and to what extent one might expect the adsorption to be specific and unpredictable.

Because data of this sort were not available the work here reported was done. This consisted in a study of the adsorption from solution of a series of pure organic compounds on the hydrous oxides of silicon, iron and aluminum and (because of its previous use as an adsorbent for organic bases) fuller's earth.

Preparation of **Adsorbents.**—The behavior of the hydrous oxides as adsorbents depends largely on the method of their preparation. Impurities on the adsorbents and the heat treatment of the adsorbents affect greatly the extent of adsorption on them. The adsorbents used in the work here reported were prepared according to methods previously used by other workers.

The silica was prepared by precipitating silicic acid and ferric hydroxide together by adding a solution of ferric chloride to a diluted solution of water glass After the precipitate was dried the ferric hydroxide was dissolved out by treatment with 6 *N* hydrochloric acid. The remaining hydrated silica was then washed by decantation with water until the water in which the silica had soaked for several hours gave no precipitate with silver nitrate. When this silica was dried and heated to 120° for several hours a very superior adsorbent resulted. Before use it was ground fine enough to pass through a 200-mesh sieve. This method of preparation was devised by Holmes and Anderson.[1]

The alumina was prepared according to the method described by Willstätter[2] for the preparation of his type B. A solution of aluminum sulfate was added slowly to a strong (20%) solution of ammonium hydroxide. The precipitate was washed four times by decantation with water and was then treated with ammonium hydroxide again, after which it was washed by decantation and then by filtration until free of sulfate ions. The product was dried at 120° for an hour and then ground and passed through a 200-mesh sieve.

The hydrous ferric oxide was prepared in a manner analogous to that used for the preparation of the alumina except that ferric chloride was used instead of aluminum sulfate.

The fuller's earth used was similar in appearance and general behavior as an adsorbent to the English earth marketed by Eimer and Amend, but its exact history is unknown.

Choice of Compounds for Adsorption.—An attempt was made to select a group of organic compounds of widely different chemical properties, both as to acidic and basic strengths and also as to molecular structure and complexity. The choice of compounds for this study was limited to those which are sufficiently soluble and to those which were available in pure form. Eighteen organic compounds, listed in the table, varying in acidic and basic strengths from aspartic acid, having a dissociation constant of $k_a = 1.4 \times 10^{-4}$, to piperidine, having a dissociation constant of $k_b = 1.2 \times 10^{-3}$, were finally chosen. Most of these substances are of biological importance. All except glucose contain nitrogen.

Carrying Out of Adsorption and Analysis.—Solutions of eighteen organic compounds in 0.01 M concentration were prepared and 25cc. samples of these solutions were shaken in a mechanical shaker for five minutes

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[1] Holmes and Anderson, *Ind. Eng. Chem.*, 17, 280 (1925).

[2] Willstatter, *Ber.*, 56, 149 (1923).

with 0.5 g. of the dried adsorbent which had been ground and passed through a 200-mesh sieve. The solution was then filtered from the adsorbent through filter paper in a Gooch crucible and analyzed for the amount of the compound left in the solution. The methods of analysis were different for the different types of compounds studied. Those compounds which were not volatile at 100°, the temperature of the drying oven, were analyzed simply by evaporating 10 cc. of the filtrate *to* dryness in a weighed crucible and weighing the non-volatile material. Any of the adsorbent that might have come through the filter was taken account of by igniting the material and weighing the crucible plus the non-combustible residue. Those compounds which are distinctly acidic or basic could be titrated and this method was used wherever possible. Some of the nearly neutral compounds were volatile at the temperature of the oven and the solutions of these compounds could not be analyzed by either of the two above methods. Since all of these compounds contained nitrogen the filtrates were analyzed as to their nitrogen content by means of the micro-Kjeldahl method as modified by Koch and McMeeken[3] in which hydrogen peroxide is used as an oxidizing agent.

Whenever results were doubtful or unexpected they were checked at least approximately by using more than one method of analysis. Control experiments showed that adsorption by the small filter used was too small to affect the results detectably, and evaporation during the filtration was shown to be too small to change the results appreciably. Bacterial contamination of the solutions was avoided by using only fresh solutions in case of compounds which might be attacked by micro-organisms. The adsorbents were kept in stoppered containers and the parallel adsorption experiments were all carried out within a short time so that the adsorbents would be uniform for the different tests.

Results and Discussion.—In Table I are given the results obtained in these experiments. The PH values listed were determined directly in the case of the more nearly neutral compounds and were calculated from the ionization constants in the case of the stronger acids and bases. The values apply to the 0.01 M solutions of the pure substances used in the experiments. The following facts should be noted from a consideration of the results: (1) the adsorption by silica seems to be roughly proportional to the basic strength of the compound adsorbed. This is in keeping with the acidic character of silica. The negative adsorption noted in several cases was due to the selective adsorption of water and the consequent increase in concentration of the solution. (2) Adsorption by alumina is most marked in the case of the acidic compounds, though the most basic substance, piperidine, is also adsorbed very appreciably. These results are not unexpected in view of the well-known amphoteric charac-

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[3] Koch *and* McMeeken, THIS JOURNAL, **46,** 2066–2069 (1924).

ter of alumina. (3) Although the hydrous iron oxide used was apparently an excellent absorbent, the adsorption was very irregular, being strongest in the case of acid substances, as might be expected, but also taking place markedly in the case of certain of the neutral and basic compounds. (4) The adsorption by fuller's earth parallels very roughly the adsorption by silica. One striking exception appears in the case of caffeine. Approximately eight times as much of this substance is adsorbed by fuller's earth as by silica. (5) All of the adsorbents chosen have, rather surprisingly, adsorbent properties of about the same order, in spite of their different characters and sources.

TABLE I

RESULTS OF ADSORPTIONS

Substance	P_H	By silica, %	By alumina, %	By iron oxide, %	By fuller's earth
Piperidine	11.46	94.5	5.7	25.2	73.8
Nicotine	10.6	87.3	1.5	2 2	43.7
Arginine	9.5	72.5	1.2	34.2	31
Quinoline	8.6	47	2	1	71.2
Adenine	8.4	10.6	2	00	21.2
Caffeine	7.8	11.2	0.5	0.0	87
Creatine	7.2	4.7	1.3	3	7.42
Betaine	7.5	5.5	0	0 0	5.08
Acetanilid	7.2	2.37	1.8	12 3	3.05
Urea	7.1	1.9	2.94	0.3	5
Acetamide	7.1	1.1	3.7	1	5.4
Glucose	7.1	0.7	1.0	11.0	0.0
Succinimide	6.0	.7	0.5	0.0	.5
Glycine	6.1	.7	3.0	15 85	.0
Vicine	6.0	.7	13.85	20.25	2.86
Asparagine	5.4	.7	10.95	44.77	.0
Glutamic acid	3.2	.6	74.3	81.6	.0
Aspartic acid	3.1	.0	84.5	87.5	.0

In order to throw some light on the irregularity of adsorption by hydrous iron oxide, another sample was prepared, using an entirely different method. Ferric chloride, which is not obtainable in very pure form, was used for the preparation of the sample used above. For a second iron oxide preparation, pure electrolytic iron was oxidized by ozone in the presence of water, using a piece of platinum foil as a catalyst. The oxidation proceeded slowly but eventually a sample of hydrous iron oxide was obtained. This was heated and screened as in the former cases and tested on several solutions similar to those used above.

The results indicated in Table II show that the second sample of hydrous oxide was not, in general, as good an adsorbent as the precipitated hydrous oxide. This result is not surprising, but it is surprising to note that there is no parallelism in the behavior of the two samples toward the compounds tested. The large differences obtained emphasize the difficulty and irregularities which are liable to be encountered because of the variation in the quality of the adsorbent.

TABLE II

RESULTS WITH SECOND IRON OXIDE SAMPLE

Compound adsorbed	Adsorbed by Sample No. 1. %	Adsorbed by Sample No. 2, %
Piperidine	25.2	19.6
Nicotine	0.2	2.7
Arginine	34.2	15
Quinoline	1	22.9
Glutamic acid	81.6	15.53
Aspartic acid	87.5	14.9

Further experimentation on the effects of different factors on adsorption of organic compounds is contemplated for the future.

Summary

The extent to which eighteen pure organic compounds are adsorbed from 0.01 M solutions on the hydrous oxides of silicon, aluminum and iron and on fuller's earth has been determined. It is found that the extent of adsorption on silica of the compounds used is roughly proportional to their basic strengths, and roughly proportional to their acidic strengths in the case of adsorption on alumina. Adsorption by hydrous iron oxide was very irregular, possibly due to impurities on the adsorbent. The extent of adsorption by fuller's earth was somewhat similar to the adsorption by silica, but in a few cases there was no parallel.

EUGENE, OREGON

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

THE INTERNAL PRESSURE OF LIQUID CARBON DIOXIDE FROM SOLUBILITY MEASUREMENTS

BY ELTON L. QUINN[1]

RECEIVED OCTOBER 28, 1927 PUBLISHED MARCH 7, 1928

In a previous paper[2] on the surface tension of liquid carbon dioxide it was found that carbon dioxide had an internal pressure much the same as carbon tetrachloride, toluene and chloroform. This was determined by comparing the total energy of surface formation with the values found for these compounds, according to the method of Hildebrand.[3] It seemed desirable to check these results with the solubility data of liquid carbon dioxide but it was found that the few determinations[4,5] of a quantitative

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[1] On sabbatical leave from the University of Utah.

[2] Quinn, THIS JOURNAL, 49, 2704 (1927).

[3] Hildebrand, "Solubility," Chemical Catalog Company, New York, 1924, p. 111.

[4] Thiel and Schulte, *Z. physik. Chem.*, 96,328 (1920).

[5] Büchner, *ibid.*, 54, 665 (1906).

nature available did not lend themselves readily to a calculation of this kind. It was thought best, therefore, to make a series of determinations using naphthalene and iodine as solutes and if possible to apply the method of Hildebrand[6] in calculating the relative internal pressure of the solvent.

Experimental Procedure

Fig. 1 is a drawing of the reaction tube in which the solubility determinations were made. It will be noted that this type of reaction tube is essentially the same as that ordinarily used for liquid ammonia, the slight modifications being made to increase the strength and to facilitate handling in the thermostat. These tubes were made of soft glass tubing having an internal diameter of about 8 mm. and a 2mm. wall. The connecting tube between the measuring and reaction tubes had an internal diameter of about 4 mm. It was found that a smaller tube at this point did not work satisfactorily as it prevented the free passage of the liquid from one tube to the other. The tube was carefully cleaned with a boiling solution of sulfuric and nitric acids, then washed and dried. A plug of glass wool was placed in the end of the leg designed for the solute and the proper quantity of solute introduced. Both legs were then sealed, great care being taken to keep the flame away from the open ends. The measuring tube was then graduated, the graduation marks being etched into the glass with a solution of hydrofluoric acid.

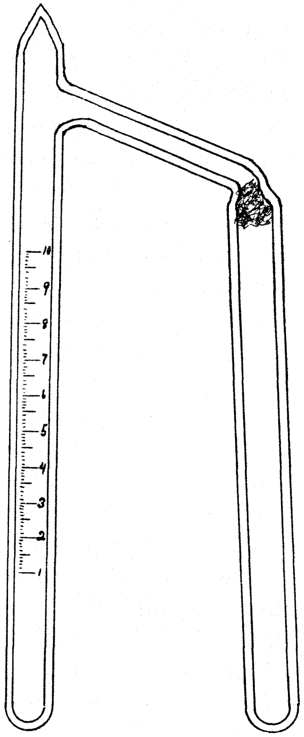

Fig. 1.

The method of introducing the liquid carbon dioxide into the tubes was essentially the same as that described in connection with the surface tension measurements.[2] In this case, however, the calcium chloride drying tower was made from an iron pipe 6.4 cm. in diameter by 56 cm. high. A safety valve fitted to the top of the tower made it possible to admit the gas to the reaction tube under any pressure up to the saturation pressure of liquid carbon dioxide.

Equilibrium between the solution and the solute was obtained by pouring the liquid carbon dioxide into the reaction tube and causing it to flow backwards and forwards over the solute for six to eight hours while it was kept at constant temperature in a thermostat. The thermostat was provided with a mechanical arrangement which kept the contents

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[6] Nildebrand, *Proc. Nat. Acad. Sci.*, *13*, *No.* 5,267 (1927).

of the tubes agitated during the time required to reach equilibrium. It was found in preliminary tests that tubes agitated one, two or three hours gave practically the same solubility; it was therefore assumed that a run of six or seven hours would be sufficient to reach equilibrium in all cases.

The naphthalene solution was, of course, colorless but the iodine solution was of a beautiful violet color. This latter fact is of some importance as it indicates the absence of solvation in the iodine solutions and places carbon dioxide in the class with "regular" solvents.

A few minutes before the end of each run the solubility tube, which had been hanging with the reaction leg below, was turned over so that the measuring leg came underneath and the agitation was continued until all of the solution had run into this part of the apparatus. Rubber gloves were worn whenever any of the tubes were handled in order to protect the hands in case one exploded and also to prevent any temperature change in the solutions. When the tube was removed from the thermostat the height of the liquid was quickly read and it was then placed in a freezing mixture and allowed to remain until the solution had frozen to a solid mass. A small hole was then melted in the top of the measuring tube and it was allowed to remain in the freezing mixture until the whole system had reached room temperature, which usually took from twenty-four to thirty-six hours depending upon the amount of solid carbon dioxide in the freezing mixture. When the tube was removed from the ether-bath the solute was found in beautiful crystals in the bottom of the measuring leg. The measuring tube was then sealed off from the rest of the apparatus and preserved until a convenient time for analysis.

The amount of naphthalene in each solution was determined by weighing the solid left after the solvent had evaporated. The iodine was determined by washing it out of the measuring tube with a strong solution of potassium iodide and titrating with a standard solution of sodium thiosulfate. The solution volume was found by filling the tube with water to the mark reached by the solution and weighing. From the weight of water the volume of the solution was calculated.

The operations described above gave the weight of solute and the volume of the solution. This was, of course, not sufficient to calculate the solubility of these substances in terms of their mole fractions. The densities of the solutions were determined by means of the special type of pycnometer shown in Fig. 2. In this tube was placed a definite quantity of the solute just sufficient to saturate the solution and leave a slight excess at the highest temperature at which readings were to be made. Liquid carbon dioxide was then admitted and the amount carefully adjusted so that it would nearly fill the tube at the highest temperature of the laboratory. It was very important that the liquid did not completely fill the tube as this condition always resulted in an explosion. After weighing the pycnometer and its contents, it was placed in a thermostat and the height of the meniscus determined at several temperatures. The solution was then frozen and the tube opened by melting a very small hole in the tip. After the solvent had evaporated at a low temperature, the tube was weighed. The difference between this weight and the weight of the tube plus contents gave the weight of the carbon dioxide in the liquid and gaseous state. The solute was then washed cut and the tube again weighed after drying. The difference between this and the previous weight gave the weight of the solute. The tube was then calibrated to the marks reached at the various temperatures. Subtracting from the total weight of carbon dioxide the weight of the vapor, which was calculated by means of Amagat's[7] values, and correcting for the small amount of undissolved solute, the weight of the solution was obtained. In this manner it was possible to determine the density of the solution over a range of about eight degrees. It was not possible to make these determinations much below the temperature of the laboratory on account of the difficulty of keeping the temperature of the tube below the danger point during the weighing operation.

The question arose as to whether the density tubes had the same volume when filled with liquid carbon dioxide, exerting a pressure of 50 to 60 atmospheres on the inside, that they had after the carbon dioxide had been removed. In order to test this point a side tube was sealed onto a test-tube and then bent into a shape something like the letter S. This was filled with distilled water until it overflowed through the side tube. The pycnometer filled with carbon dioxide was then carefully lowered to the bottom of the test-tube and the water overflowing through the side tube was collected in a weighing bottle and weighed. This was repeated several times and the carbon dioxide was then discharged and several more readings were taken sometimes several days apart in order to give the glass time to regain its former condition. In no case could a difference greater than the experimental error be detected, and as the volume of the tube could be determined within less than 0.1% the change in the tube, if any, must be smaller than this and could, of course, be neglected in this work.

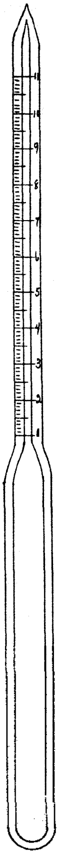

Fig. 2.

The densities of the solutions at lower temperatures were determined in the following manner. First, the solubility curve was constructed by plotting the weight of solute obtained from a definite volume of solution against the temperature and extrapolating to zero concentration. This gave the point where the density of the solution became the same as the

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[7] Amagat, Ann. *chim.* phys., [6] **29,** [68] (1893).

pure solvent. Then on large scale cross section paper the density curve of the pure solvent was constructed using the density values of Behn[8] and Jenkin.[9] The experimental densities of the solutions were plotted beside this curve for the pure solvent and curves constructed which cut this solvent curve at the temperature where the concentration of the solute became zero. These solution curves came so close to the curve of the pure solvent that no great accuracy was necessary at the junction point. The values read from these curves are shown in Table I.

TABLE I

VALUES READ PROM THE CURVES

Temp.. °C.	Density, pure solvent	Density, naphthalene solution	Density, iodine solution
25	0.710	0.740	0.720
20	.770	.790	,775
15	.816	833	.822
10	.858	.872	.863
5	.896	.906	.898
0	.927	.938	,929
− 5	.955	.967	.957
−10	.981	993	.982
−15	1.005	1.018	1,006
−20	1 031	1 040	1.031

Purification of Material

The carbon dioxide used in these determinations was obtained from commercial cylinders of the liquefied gas manufactured by the Pure Carbonic Company of Berkeley, California The analysis of the gas showed a purity of 99.85% of carbon dioxide with a trace of water vapor when the sample was taken from the top of the cylinder. Although oil was found when the gas was taken from an inverted tank, no evidence of it was ever found when the sample was taken from the top of the cylinder.

The naphthalene used was Baker's Analyzed, Lot No. 4425, with a melting point of 79". This was fractionally distilled several times, the middle fraction only being collected from each distillation. This was crystallized from redistilled alcohol twice and dried in a desiccator for several weeks. The freezing point of the purified naphthalene was then determined by taking the cooling curve of a large sample in a test-tube. Several determinations gave values between 79.9 and 80.2" with an average of 80°. The iodine used was also Baker's Analyzed. This was resublimed once in the presence of potassium iodide before it was used.

The results obtained from these solubility determinations are shown in Tables II and III.

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[8] **Behn, Ann.** *Physik, [4B,733 (1900).*

[9] **Jenkin,** *Proc. Roy. Soc. (London),* 98A, *170 (1920).*

TABLE II

SOLUBILITY OF NAPHTHALENE IN LIQUID CARBON DIOXIDE AT VARIOUS TEMPERATURES

Det. no.	Temp., °C.	Vol. of CO_2 soln., cc.	Wt. of CO_2, g.	Wt. of $C_{10}H_8$ found, g.	Wt. of $C_{10}H_8$ per mole of CO_2, g	Av. weight, g.	Mole frac.	Log *N*
1	25	3.387	2.456	0.0502	0.8993			
2	25	4 044	2 932	0600	.9004			
3	25	6 822	4 946	.1016	.9038	0 901	0 00698	−2.156
4	20	4.851	3.760	.0722	.8449			
5	20	4.935	3.823	.0748	.8609			
6	20	6.054	4.691	.0913	.8563	.854	.00662	−2.179
7	10	2.481	2.131	.0316	.6525			
8	10	5.817	4.996	.0758	.6675			
9	10	3.105	2.667	.0397	.6549	.658	.00511	−2.292
10	0	6.726	6.241	.0678	.4780			
11	0	4.918	4.563	.0501	.4831			
12	0	4.672	4.335	.0469	.4760	.479	.00372	−2.429
13	−21	4.631	4.809	.0255	.2333			
14	−21	3.038	3.156	.0165	.2300			
15	−21	5.379	5.586	.0291	.2292	.231	.00180	−2.745

TABLE III

SOLUBILITY OF IODINE IN LIQUID CARBON DIOXIDE AT VARIOUS TEMPERATURES[a]

Det. no.	Temp., °C.	Vol. of CO_2 soln., cc.	Wt. of CO_2, g.	Wt. of *It* found, g.	Wt. of I_2 per mole of CO_2, g.	Av. weight, g.	Mole frac.	Log *N*
1	25	5.140	3.700	0.0075	0.0900			
2	25	3.860	2.779	.0058	.0931	0.0915	0.000361	−3.442
3	20	5.002	3.876	.0068	.0772			
4	20	8.229	6.377	.0112	.0777	.0774	.000305	−3.515
5	10	4.273	3.688	.0044	.0520			
6	10	4.106	3.543	.0043	.0533	.0526	.000207	−3.683
7	0	5.451	5.064	.0039	.0343			
8	0	4.561	4.237	.0033	.0350	.0347	.000136	−3.864
9	−11.4	3.360	3.322	.0014	.0191	.0191	.0000753	−4.123
10	−21	3.493	3.615	.00089	.0105			
11	−21	4.715	4.880	.00111	.0100	.0102	.0000405	−4.392

[a] This is the second set of iodine determinations made. The agreement between the averages in the two sets was quite satisfactory but the agreement between the individual measurements in the first set was not.

Discussion of Results

The relation between the internal pressure of a solvent and the deviation of its solutions from Raoult's law has been discussed in detail by Hildebrand.[10] He points out that one of the most important methods of estimating internal pressure differences between various solvents is to plot their solubility curves for the same solute (log N_2 against $1/T$) with the curve of the ideal solvent. The displacement of these curves from

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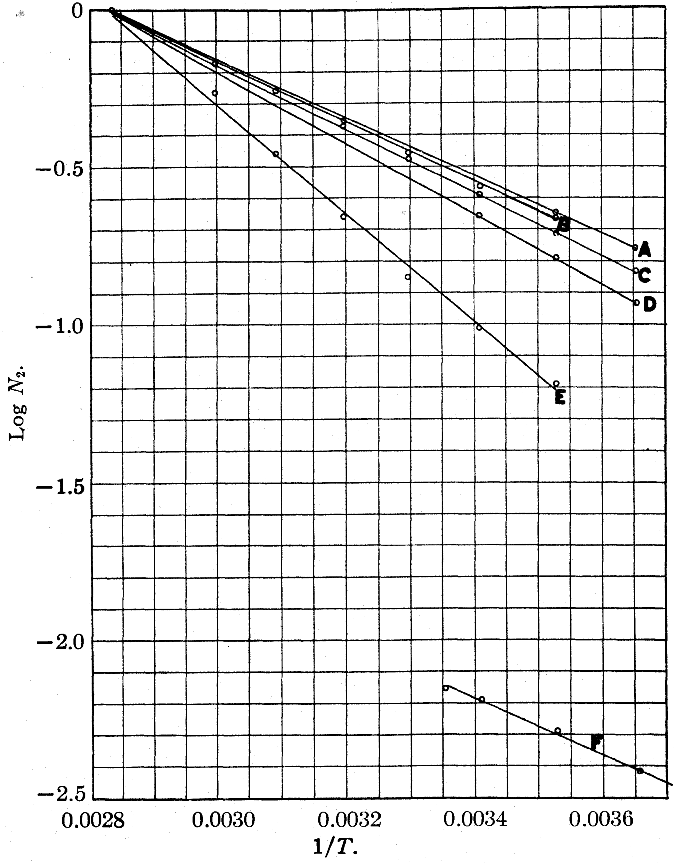
[10] **Ref. 3,** p. 115.

that of the ideal solution is a measure of their internal pressure differences and from such a plot it is possible to arrange the solvents in an internal pressure series. This method has the disadvantage of requiring the plotting of the curves before the position of any solvent in the series can be assured and in addition lacks quantitative significance. Recently Hildebrand[6] developed an equation by means of which this deviation can be calculated quantitatively for what he calls regular solvents and which has the added advantage that the approximate internal pressure factor can be calculated from a single solubility measurement.

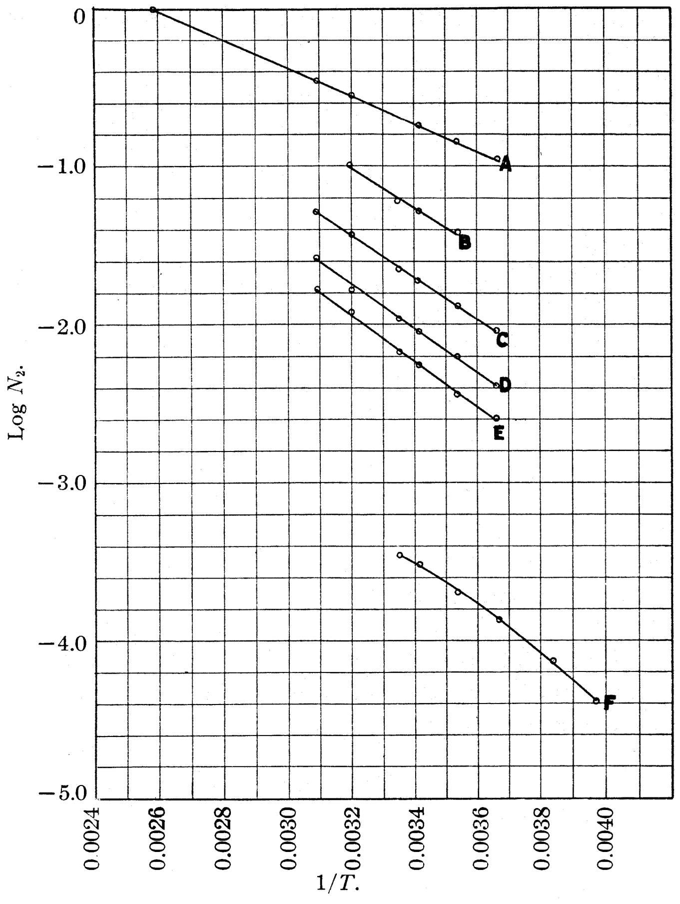


A, ideal; B, C_6H_5Cl; C, C_6H_6; D, CCl_4; E, C_6H_{14}; F, CO_2.

Fig. 3.—Solubilities of naphthalene.

The Hildebrand equation may be written in the following form, $\ln N_2^R/N_2 = bN_1^2/RT$, in which N_2^R and N_2 are mole fractions of the ideal and experimental solubilities of a solute, respectively, at the absolute temperature T, while N_1 is the mole fraction of the solvent, b is a constant which is related to the difference in internal pressure for the two components and R the usual gas constant or 1.99. The ideal solubility of N_2^R can be calculated from the heat of fusion and melting point of the solute.

Ward[11] has made solubility determinations of naphthalene in a number of solvents and Fig. 3 shows a few curves plotted from his data together with the curve for the solubility of naphthalene in carbon dioxide. This gives a clear idea of the relation of carbon dioxide as a solvent to the more common solvents and indicates that the internal pressure of liquid carbon dioxide is very low. Fig. 4 plotted in the same manner from data given by Hildebrand shows the solubility of iodine in various solvents. This also indicates that carbon dioxide has a very low internal pressure.



A, ideal; B, $CHBr_3$; C, $CHCl_3$; D, CCl_4; E, C_7H_{16}; F, CO_2.

Fig. 4.—Solubilities of iodine.

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[11] Ward, *J.* Phys. Chem., 30, 1327 (1926).

If we write the Hildebrand equation as $(T \log N_2/N_2^R)/N_1^2 = k$ and calculate the value of k for the solutions of naphthalene and iodine in liquid carbon dioxide at different temperatures, we obtain the results indicated in Tables IV and V.

TABLE IV

DATA FOR NAPHTHALENE

$\log N_2^R$	$\log N_2$	N_2	T	k
−0.490	−2.156	0.00698	298	499
− .542	−2.179	.00662	293	485
− .647	−2.292	.00511	283	469
− .764	−2.429	,00372	273	458
−1.033	−2.745	,00180	252	433
			Average	469

TABLE V

DATA FOR IODINE

$\log N_2^R$	Lon N_2	N_2	T	k
−0.673	−3.442	0.000361	298	827
− .723	−3.515	.000305	293	820
− .829	−3.683	.000207	283	807
− .942	−3 864	.000136	273	800
−1 075	−4.123	.0000753	262	800
−1.200	−4 392	.0000405	252	805
			Average	810

In order to show the relation of these values of k to the average value obtained for other solvents, Table VI has been arranged, in which the solvents have been placed in the increasing order of their internal pressures. The data from which these values of k were calculated were taken from the determinations made by Ward and the tables published by Hildebrand. In the series of solvents of naphthalene the value of k was calculated at five degree intervals over a range of temperature from 0 to 25°, while the series of solvents for iodine were calculated at ten degree intervals from 0 to 50°.

TABLE VI

INTERNAL PRESSURE SERIES

Naphthalene as solute		Iodine as solute	
Solvent	**k**	**Solvent**	**k**
Carbon dioxide	469	Carbon dioxide	810
Carbon tetrachloride	57	Heptane	450
Toluene	30	Carbon tetrachloride	393
Benzene	26	Chloroform	302
Chlorobenzene	8	Bromoform	178
Nitrobenzene	23		
Acetone	74		
Aniline	122		

Internal Pressure from Surface Tension Measurements

When an attempt was made to evaluate the internal pressure of carbon dioxide from the surface tension measurements there was much doubt as to the best way to accomplish this. The total energy of surface formation was calculated by means of the Thomson equation and a value of 62 was obtained. This indicated that carbon dioxide had an internal pressure much the same as carbon tetrachloride, toluene and chloroform. In the light of these solubility determinations it is readily seen that this comparison is very misleading, as carbon dioxide has a very much lower internal pressure than any of these compounds. It is now clear that some other unit of comparison should have been used and if we calculate the value of $\gamma/V^{1/3}$ at 20° we obtain a value of 0.35, which places carbon dioxide in the internal pressure series in a position more nearly in accord with that obtained from solubility determinations. A more exact comparison at this time is not feasible.

Summary

1. A method has been described for determining the solubility of solids in liquefied gases, which can be applied to liquids having very high vapor pressures.
2. The solubility of naphthalene and iodine in liquid carbon dioxide has been determined over a range of temperature from 25 to —21°.
3. The position of liquid carbon dioxide in the internal pressure series has been determined. This indicated that this compound has an internal pressure much less than those liquids commonly used as solvents.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

THE STANDARDIZATION OF SILVER NITRATE SOLUTIONS USED IN CHEMICAL STUDIES OF SEA WATERS[1]

BY THOMAS G. THOMPSON

RECEIVED NOVEMBER 1, 1927 PUBLISHED MARCH 7, 1928

The advantages of the use of standard sea water prepared by the Hydrographic Laboratories of Copenhagen have been pointed out by Knudsen.[2] This standard water has been used for over a quarter of a century for the evaluation of silver nitrate solutions employed in oceanographic investigations and is obtainable only from the Hydrographic Laboratories. However, Bertrand, Freundler and Ménager,[3] Ménager[4] and Giral[5] have recently criticized this standard and the two latter authors have recommended the use of sodium chloride.

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[1] Presented before the Division of Water, Sewage and Sanitation at the 74th meeting of the American Chemical Society, Detroit, Michigan.

[2] Knudsen, *Publications de circonstance*, No. 2 (1903); No. 87 (1925).

[3] Bertrand, Freundler and Ménager, *Compt. rend.*, 174, 1251–1253 (1922).

[4] Ménager, *ibid.*, 179, 195–198 (1924).

[5] Giral, *Publications de circonstance*, No. 90 (1926).

To properly carry out the determination for the halide ions, as recommended by the International Council for the Study of the Sea, standard sea water is necessary and the titer tables[6] are essential, while the special pipets and burets provided by the Hydrographic Laboratories are recommended. The chlorides[7] are calculated as grams of chlorine per kilo ($^0/_{00}$) and by the use of the Hydrographical Table the salinity[8] may be readily ascertained.

The use of standard sea water and the special apparatus produces unnecessary inconveniences because of the time required for procurement. The substitution of common volumetric apparatus, made to meet the specifications of the United States Bureau of Standards, and of pure sodium chloride solutions gives results that are just as accurate.

Experimental

Standardization of Silver Nitrate Solution.—The Mohr method, using potassium chromate solution as an indicator for the determination of chlorine, is generally accepted as the standard method in oceanographic and thalassographic chemistry. A comparison of this method with that of Volhard's and the usual gravimetric procedure has recently been made by Smith and Thompson[9] in which the general agreement of the three methods as applied to sea water was demonstrated.

Two methods for standardizing the silver nitrate solution were used, (1) pure sodium chloride and (2) standard sea water from the Hydrographic Laboratories.

1. The sodium chloride was prepared by treating a filtered saturated solution made from Merck's blue label salt with hydrogen chloride. The precipitated crystals were dried, a saturated solution was made and from this the salt was precipitated with alcohol. The crystals were finally dried at 150°. Liter solutions of sodium chloride were then prepared equivalent to (a) 17.409 g. and (b) 19.411 g. of chlorine for silver nitrate solution No. 1 and (c) 19.409 g. of chlorine for silver nitrate solution No. 2. Twenty-five cc. of these solutions were pipetted into casseroles and titrated with the silver nitrate solution. Titration in a yellow light facilitated the observance of the end-point.

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[6] "Hydrographical Tables," edited by Martin Knudsen, Copenhagen, 1901.

[7] The amount of chlorine in sea water is universally defined as the grams of chlorine contained in one kilogram of water, assuming the small quantities of bromine and iodine to be replaced by chlorine.

[8] The salinity has been correlated with chlorine by Knudsen, Sørensen and others and is expressible in the formula, $S = 0.03 + 1.805\ \mathrm{Cl}$. It is defined as the weight in grams of all the salts dissolved in a kilogram of sea water, after the carbonates have been converted to oxides, the bromine and iodine have been replaced by chlorine and the organic matter has been completelv oxidized.

[9] Smith and Thompson, *University of Washington Eng. Expt. Sta. Bull., No. 41,* 38–41 **(1927).**

2. Two tubes of standard sea water at 20° were opened and 25cc. portions immediately pipetted and titrated. The samples, according to the analysis of the Hydrographic Laboratories, contained 19.386 and 19.379 g. of chlorine per kilo, respectively, and the calculated densities at 20° were 1.021280 and 1.02478. The standard sea water thus contained 19.867 and 19.859 g. of chlorine per liter at 20°.

Ordinary pipets and burets calibrated by the United States Bureau of Standards for 20° were used. A temperature of 20° for titration has been found by the author to be more desirable than that of 15° both for work in the laboratory and on board ship.

The results of the standardization of two silver nitrate solutions are shown in Table I.

TABLE I

STANDARDIZATION OF SILVER NITRATE SOLUTION AT 20°

	1 cc. of $AgNO_3$ equiv. in mg of Cl	
	No. 1	No. 2
Sodium chloride (a)	10.067	....
Sodium chloride (b)	10.070	. .
Standard sea water	10.072	....
Sodium chloride (*c*)	....	0.9855
Standard sea water	....	.9853

The above results show that the standardization of the silver nitrate solution may be accomplished with the same result using either standard sea water or pure sodium chloride and that the salts other than chlorides present in the sea water have no effect upon the titration. The latter statement confirms the work of Giral[5] with synthetic sea waters. Thus pure sodium chloride, which is readily obtainable, may be used as a standard. It is suggested that liter solutions of sodium chloride approximating the concentration of chlorine in the sea waters under investigation be utilized and that in all cases 25cc. samples at 20° be taken for titration. The grams of chlorine per liter at 20° of water are thus calculated from the data given by the titration.

In order to arrive at the relation between the chlorine per liter at 20° and the chlorine per kilo, the data in Table II were calculated from the

TABLE II

DATA FROM WHICH EMPIRICAL FORMULA WAS CALCULATED

Grams of chlorine per liter at 20°, Cl_v	Grams of chlorine per kilogram, Cl_w	Cl_v − 14 244	Cl_w − 14.000	$\frac{Cl_w - 14\ 000}{Cl_v - 14.244}$
14.244	14.000	0	0	0
15.282	15.000	1038	1000	.96340
16.322	16.000	2078	2000	.96246
17.366	17.000	3122	3000	.96092
18.412	18.000	4168	4000	.95969
19.461	19.000	5217	5000	.95844
20.513	20.000	6269	6000	.95709

Hydrographical Tables and the following empirical formula was derived, where Cl_v represents the grams of chlorine per liter at 20° and Cl_w the grams of chlorine per kilogram of sea water.

$$Cl_w = 0.008 + 0.99980\,Cl_v - 0.001228\,Cl_v^2$$

The difference, $Cl_v - Cl_w$ shows the marked error introduced should a liter of sea water be assumed to weigh a kilogram, an assumption sometimes found in the literature.

From the above formula a table has been calculated whereby, knowing the grams of chlorine per liter at 20° of sea water, one can readily calculate the grams of chlorine per *mille*, or vice versa, and thus have a means of arriving at the desired densities.

Table III shows the corrections for reducing grams of chlorine per liter at 20° to grams per kilo at any temperature.

TABLE III

CORRECTIONS FOR REDUCING GRAMS OF CHLORINE PER LITER AT 20° TO GRAMS PER KILO AT ANY TEMPERATURE

Chlorine, g./l. at 20°	Correction	Chlorine, g./l. at 20°	Correction	Chlorine g./l. at 2do	Correction	Chlorine, g./l. at 20°	Correction
5	−0.02	9	−0.09	13	−0.20	17	−0.35
6	− .04	10	− .12	14	− .23	18	− .39
7	− .05	11	− .14	15	− .27	19	− .44
8	− .07	12	− .17	16	− .31	20	− .49

In order to test the validity of the formula, samples of water collected from various sources were analyzed both by volume and by weight. The results are given in Table IV. The samples were secured from the North Pacific off the Alaskan Coast, the Puget Sound Biological Station in the San Juan Islands, several points in Puget Sound and one sample is that of standard sea water obtained from the Hydrographic Laboratories of Copenhagen and evidently collected from the Atlantic Ocean.

TABLE IV

ANALYSES OF VARIOUS SEA WATERS SHOWING AGREEMENT WITH CALCULATED VALUES

Determined		Calcd.	
G. of Cl per liter at 20° Cl_v	G. of Cl per kilo,[a] Cl_w	G. of Cl per kilo, Cl_w	Diff.
15.66	15.38	15.37	+0.01
16.36	16.03	16.03	.00
17.40	17.03	17.03	.00
17.96	17.56	17.57	− .01
17.26	16.90	16.90	.00
19.87	19.39	19.39	.00
15.84	15.54	15.54	.00
16.54	16.20	16.21	− .01
15.72	15.49	15.42	+ .07

[a] Weighed in air.

Five of the samples were analyzed by Miss Margery Walker and Mr. Ronald Benson. Particular attention is called to the last sample in the table, as it represents the sea water taken near the mouth of a pipe discharging bleach waste from a paper pulp mill into Puget Sound. In this case by determining the grams of chlorine per liter and per kilo of sea water and converting the former with the aid of the conversion table to grams per kilo, an indication of the extent of pollution may be ascertained from the difference between the calculated and determined values for Cl_w.

The excellent agreement of the calculated results and those obtained by analyses demonstrates not only the accuracy of the tables but also of the method of analysis. The relatively high degree of precision of the analytical method is also cited by Helland-Hansen[10] and others. The suggestion of Giral[6] for increasing the permissible error recommended by the International Council for the Exploration of the sea is unwarranted.

Conclusion

1. Sodium chloride may be substituted for standard water for standardizing silver nitrate solutions to be used for oceanographic studies. Both standards give practically identical results.

2. An empirical formula has been derived and corrections have **been** calculated therefrom permitting the conversion of grams of chlorine per liter at 20° of sea water to grams of chlorine per *mille* or *vice versa.*

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

INFRA-RED ABSORPTION BY THE N-H BOND
II. IN ARYL, ALKYL AND ARYL-ALKYL AMINES

BY JOSEPH W. ELLIS

RECEIVED NOVEMBER 23, 1927 PUBLISHED MARCH 7, 1928

This paper represents a continuation of a study of the near infra-red absorption in primary, secondary and tertiary amines, Part I[1] of which was limited to an examination of aniline, five mono- and five dialkyl anilines. The present paper presents the absorption **curves** to about 2.5μ of the following compounds, all of which were bought from the Eastman Kodak Company: mono-, di- and tri-*n*-propyl-, n-butyl- and iso-amylamine; mono- (aniline), di- and triphenylamine; mono-, di- and tribenzylamine; a-, methyl-a-, dimethyl-a-, ethyl-a- and diethyl-α-naphthylamine; and *p*-, methyl-p- and dimethyl-*p*-toluidine. The primary purpose of the investigation is to test further the hypothesis advanced in

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[10] "Internat. Rev. Hydrobiol. und Hydrograph.," Hydrograph. suppl., Series I, part 2, 1912, p. 39.

[1] Ellis, THIS JOURNAL, 49, 347 (1927).

Part I that certain definite absorption bands below 3μ are associated with the N-H bond.

Two cell thicknesses, 2 mm. and 40 mm., were used with each of the liquid members of this group of compounds. The 2mm. cells were microscope depression slides with thin cover glasses. It was found that these slides, even in a vertical position, retained the liquid indefinitely without any sealing. The 40mm. cell was of glass with quartz ends of 2 mm. thickness held on by pressure exerted by threaded brass collars.

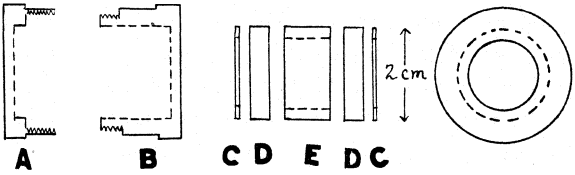

Fig. 1.—A demountable absorption cell.

The four members which are solids at room temperature, namely, di- and triphenylamine, α-naphthylamine and p-toluidine, were maintained in a molten state at temperatures just above their respective melting points. A demountable cell, 10 mm. in length, sketched in Fig. 1, was constructed for this purpose A and B are two parts of a brass housing, threaded to screw together. D, D are 4mm. quartz end-plates which fit snugly against the ground faces of the Pyrex glass cell E. C, C are steel spring washers designed to allow for the unequal expansions of brass, quartz and glass. The cell was packed with the compound which was to be examined and fitted into a well in an asbestos block, 10 X 10 X 3.5 cm., which could be raised to the desired temperature. Heat was produced in the block by maintaining a controlled current in a high resistance wire which threaded it. If the cell was not sufficiently filled after melting took place, it was cooled and more of the substance added.

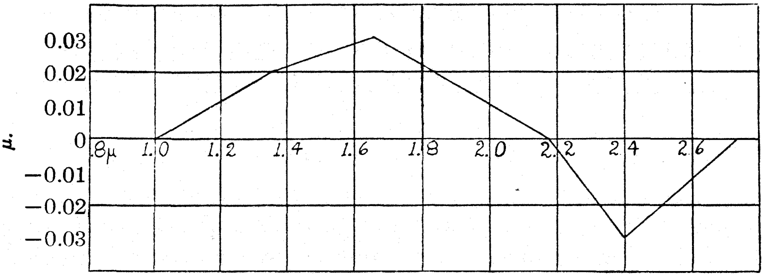

Fig. 2.—Wave length corrections to previous values.

In Figs. 3–18 are given the absorption records of the above-mentioned amines as traced by the recording spectrograph which has been used throughout this and other investigations. During another study[2] it was discovered that, because of inaccurate calibration, slight corrections must be made to many of the wave length values previously published by the author in several papers. These corrections apply to some of the values given for absorption bands in aniline and the alkyl anilines of Part I of this paper. In Fig. 2 a correction curve is given which should be used with all values previously published. Throughout this article only corrected values will be stated when quoting previous work.

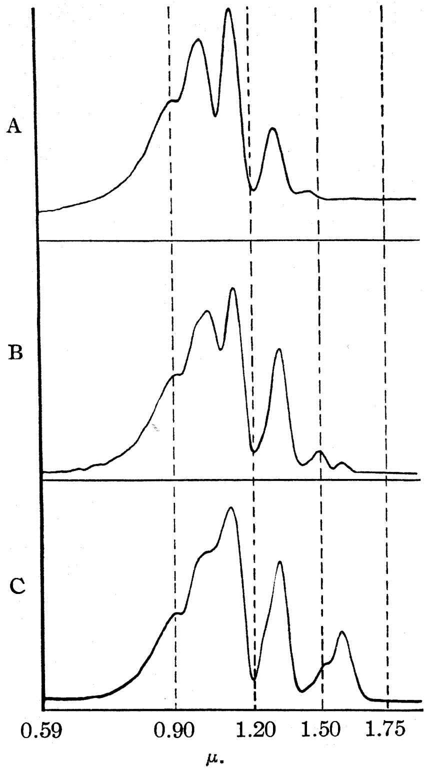

Fig. 3.—A, n-propylamine, 40 mm.; B, di-n-propylamine,40 mm.; C, tri-n-propylamine, 40 mm.

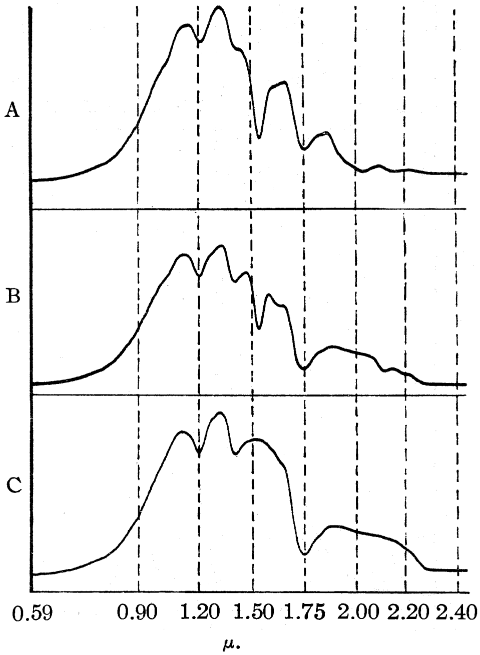

Fig. 4.—A, n-propylamine, 2 mm.; B, di-n-propylamine, 2 mm.; C, tri-*n*-propylamine (purified), 2 mm.

Absorption maxima at 1.49μ and 1.03μ[3] have been discovered in the spectra of aniline and five mono-alkyl anilines which, when taken with a strong isolated maximum discovered by Bell[4] at 2.8μ, form a parabolic series when expressed in wave numbers. The disappearance of these three bands

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[2] Ellis, *Proc. Nat. Acad. Sci.*, 13,202 (1927).

[3] *A* careful recheck of this value gives 1.03μ instead of the 1.04μ value previously given.

[4] Bell, THIS JOURNAL, 47,2192 (1925).

in the spectra of the corresponding dialkyl anilines lent support to the hypothesis advanced by the writer that these maxima represent characteristic frequencies associated with natural oscillations of the N-H pair of atoms.

Bell[5] has continued his study with four additional papers in which he has found absorption bands for numerous primary and secondary alkyl, aryl and aryl-alkyl amines analogous to the 2.8μ band in aniline and mono-alkyl anilines, varying in position from 2.9μ to 3.05μ. These are considerably diminished in the secondary amines and disappear, or practically disappear, in the tertiary amines.

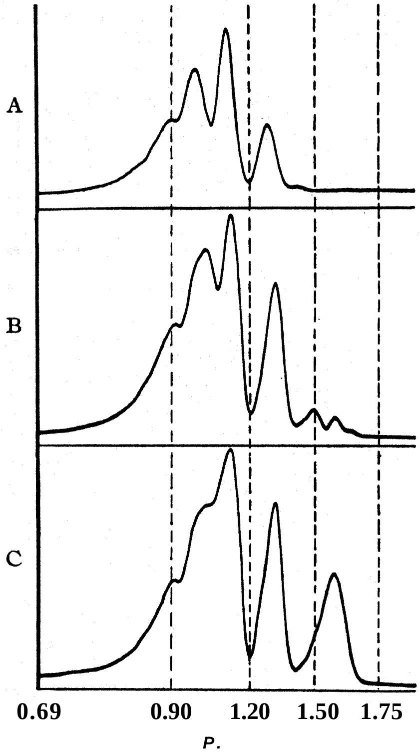

Fig. 5.—A, n-butylamine, 40 mm.; B, di-n-butylamine, 40 mm.; C, tri-*n*-butylamine, 40 mm.

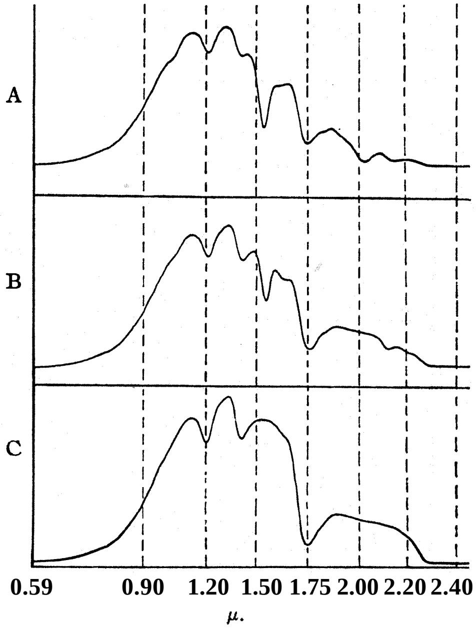

Fig. 6.—A, n-butylamine, 2 mm.; B, di-n-butylamine, 2 mm.; C, tri-*n*-butylamine, 2 mm.

In the records of the primary and secondary amines, Figs. 3–18, it is seen that there are two bands varying respectively from 1.49μ to 1.55μ and 1.03μ to 1.06~. These are analogous to the 1.49μ and 1.03μ bands of the anilines. In general it is noticed that a shift toward longer wave lengths of the band near 3μ is accompanied by a corresponding shift in the two

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[5] (a) Bell, This Journal, 47,3039 (1925); (b) 48,813 (1926); (c) 48, 818 (1926); (d) 49, 1837 (1927).

shorter wave length bands. Furthermore, these latter absorption maxima disappear in most of the tertiary amines. In the cases where they remain as traces in the original samples of the tertiary compounds they have been proved to be due to impurities, as will be pointed out later.

The records for the alkyl amines are shown in Figs. **3–8.** The bands ascribed to the N-H linkage are found at **1.54–1.55**μ and 1.06μ. These may well be interpreted as the second and third members of series analogous to that found for the anilines or, in terms of the older phraseology, as the first and second harmonics (or overtones) of the value found by Bell at 3.00–3.05μ. A trace of the 1.55μ absorption remains in the record of tri-*n*-propylamine, Fig. 3C. A portion of the original sample of this material was treated by Dr. G. R. Robertson of the Chemistry Department with the aim of removing any possible primary or secondary amines. The process adopted was similar to that used in the purification of methylethylaniline (Part I).[6] That the trace of a band present in Fig. *3C* is

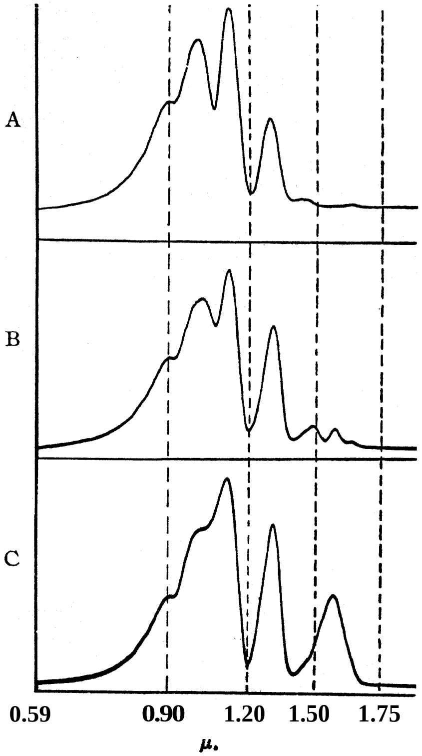

Fig. 7.—A, iso-amylamine, 40 mm.; B, di-*iso*-amylamine, 40 mm.; C, tri-*iso*-amylamine, 40 mm.

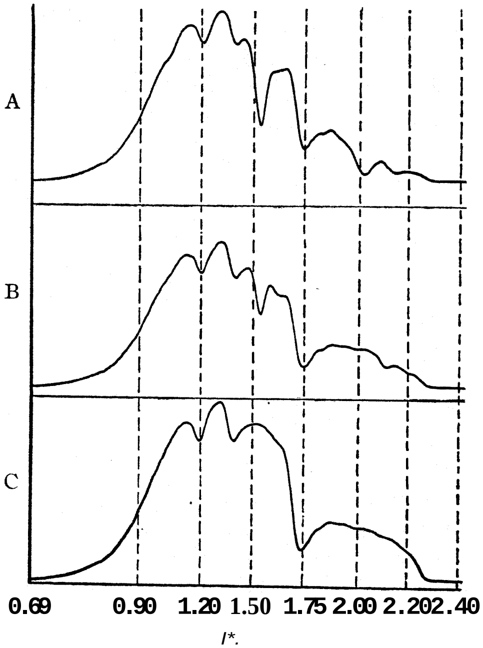

Fig. 8.—A, *iso*-amylamine, 2 mm.; B, di-iso-amylamine, 2 mm.; C, tri-*iso*-amylamine, 2 mm.

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[6] Ref. 1, p. 352.

not due to tri-*n*-propylamine is proved by its absence in the records of the treated substance, Figs. 18A and 4C.

The maxima at 1.75, 1.40, 1.20, 1.02 and 0.92μ are the established C-H bands characteristic of alkyl groups.

The 1.49μ and 1.03μ bands of aniline are found diminished in the record of diphenylamine, Fig. 9, while they are essentially lacking in the record of triphenylamine. The 1.68, 1.41 and 1.15μ maxima are C-H bands characteristic of the phenyl group.

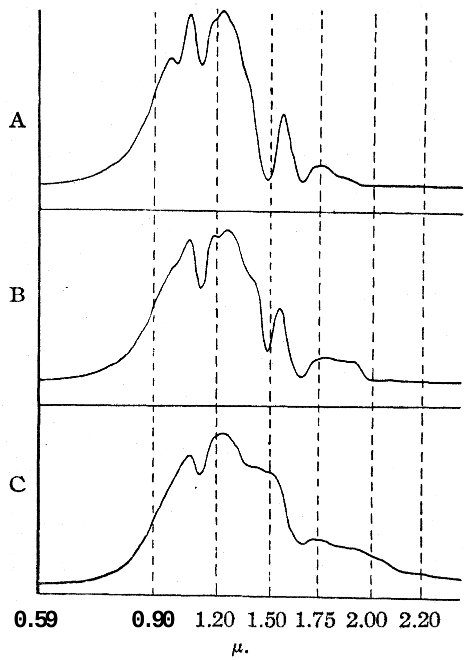

Fig. 9. —A, aniline, 10 mm.; B, diphenylamine, 10 mm.; C, triphenylamine, 10 mm.

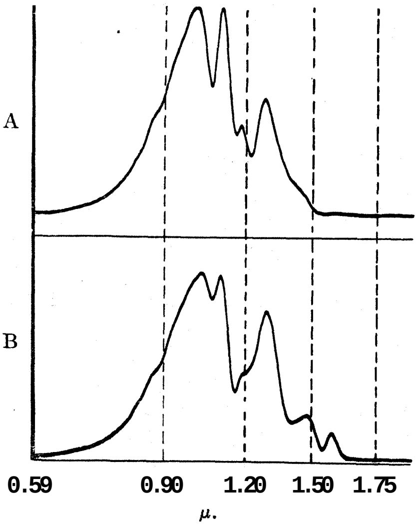

Fig. 10. —A, benzylamine, 40 mm.; B. dibenzylamine, 40 mm.

The shift toward shorter wave lengths of the absorption maxima associated with carbon-hydrogen linkages in the case of aryl compounds is doubtless to be associated with the lack of saturation in the molecules. It appears that this unsaturation also affects an amino group attached to an aryl group. Thus we have low wave length values for the N-H bands in aniline as compared with the corresponding values in the alkyl amines. In mono- and dibenzylamine, Figs. 10 and 11, where the amino group is attached to an alkyl rather than to the phenyl group, the N-H bands have the high wave length values 1.55μ and 1.06μ. The contributions of both the phenyl and alkyl C-H pairs are seen in the [1.68, 1.75μ], and possibly the [1.15, 1.20μ] regions.

In the spectra of a-, methyl-a- and ethyl-a-naphthylamine, *p*-, methyl-p- and ethyl-*p*-toluidine, Figs. 12–17, the N-H bands have the anticipated low values of 1.49–1.51 μ and 1.03 μ There are traces of the 1.49 μ band in the records of dimethyl-a- and diethyl-a-naphthylamine and dimethyl-p-toluidine. That these disappear when treated for the removal of probable primary or secondary amines is shown in the case of the last two substances in the records of Fig. 18. No attempt was made to purify dimethyl-a-naphthylamine. It is of interest to note that the tertiary amines which retain traces of the 3 μ band in Bell's records are included among the compounds which have here been shown to contain impurities.

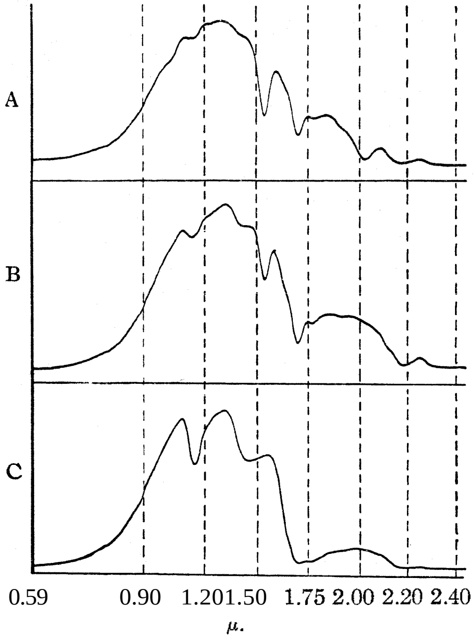

Fig. 11.—A, benzylamine, 2 mm.; B, dibenzylamine, 2 mm.; C, tri-benzylamine, 10 mm.

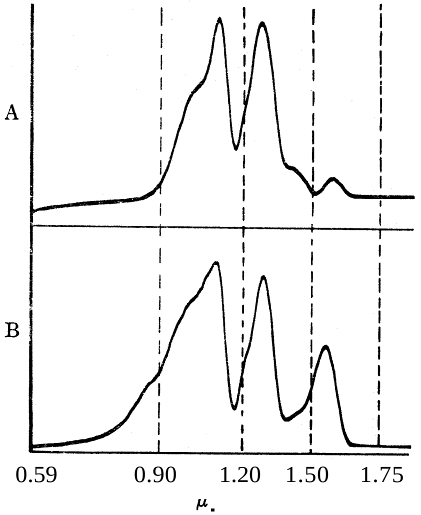

Fig. 12.—A, methyl-α-naphthylamine, 40 mm.; B, di-methyl-a-naphthylamine, 40 mm.

Bell[5d] has found a very pronounced absorption band at 6.25 μ in mono-alkyl amines, which practically disappears in the di- and trialkyl amines. He points out that his spectra of primary aryl and aryl-alkyl amines show evidence of absorption by the amino group in this region, although a band characteristic of benzene, naphthalene and their derivatives tends to make interpretation difficult.

Salant[7] has examined the spectra of certain secondary and tertiary amines in the 6.2 μ region with the definite purpose of testing his previous assumption[8] that a fundamental band characteristic of the N-H bond

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[7] Salant, *Nature*, 119, 926 (1927).

[8] Salant, *Proc. Nat. Acad. Sci.*, *12*, 74 (1926).

occurs there. He concludes that such a fundamental does not exist. The strength of the 6.25μ band, however, found by Bell in the mono-alkyl amines suggests this as a fundamental.

This band is of interest in connection with a maximum at 2.01–2.03μ observed in the spectra of primary amines in the present paper. It might be regarded as the second harmonic of the 6.25μ band, while those at 1.49–1.51μ and 1.03–1.06μ might be regarded as the third and fifth harmonics respectively. There are two arguments, however, against this interpretation: (1) the deviation from integral multiple relationship among these bands is of the wrong sense; that is, a harmonic should have a slightly longer rather than a shorter wave length than one-half, one-third, etc., of the value of its fundamental; (2) whereas the 1.49–1.55μ and 1.03–1.06μ maxima retain their positions with diminished intensities in passing to the secondary amines, the 2.01–2.03μ maximum either shifts to a longer wave length value or disappears.

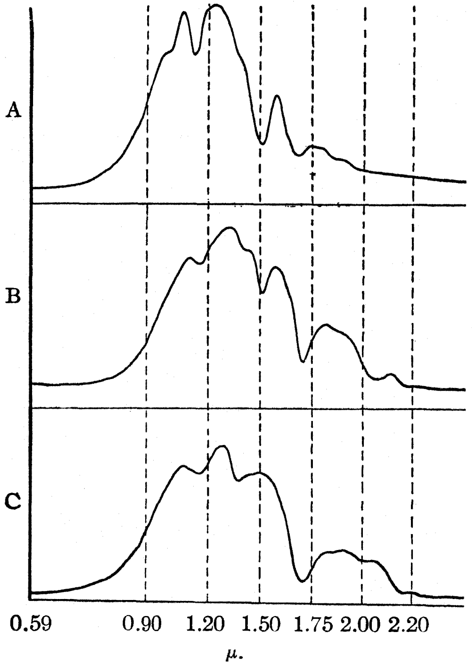

Fig. 13.—A, a-naphthylamine, 10 mm.; B, methyl-a-naphthylamine, 2 mm.; C, dimethyl-a-naphthylamine, 2 mm.

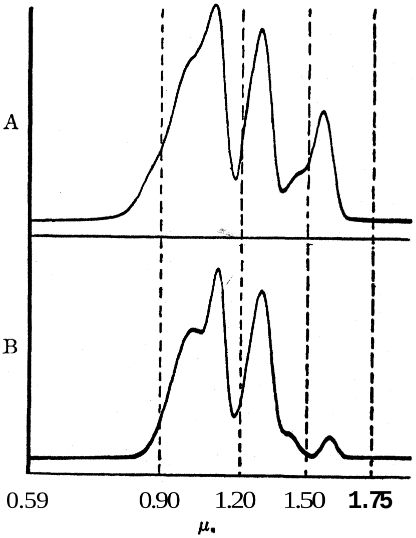

Fig. 14.—A, ethyl-a-naphthylamine, 40 mm.; B, diethyl-a-naphthylamine, 40 mm.

The writer is inclined to interpret the N-H bands in a manner analogous to his modified interpretation of the C-H bands.[2] The 6.9μ and 3.45μ bands, and the 6.75μ and 3.25μ bands, characteristic of alkyl and aryl groups, respectively. are assumed to be associated with two fundamental modes of vibration of the C-H pair. The longer wave length fundamental seems to have no harmonics, while the [1.75 (alkyl), 1.68μ (aryl)], [1.20μ, 1.15μ] and [0.92μ, 0.88μ] bands are regarded as the first three harmonics of the 3.45μ (3.25μ) fundamental. The maxima in the regions of 2.30μ (2.18μ), 1.40μ, 1.02μ and 0.83μ are interpreted as "combinations" of the 6.9μ (6.75μ) band with the 3.45μ (3.25μ) fundamental and its overtones, respectively. A combination band is one whose frequency is determined by the addition of two other frequencies.

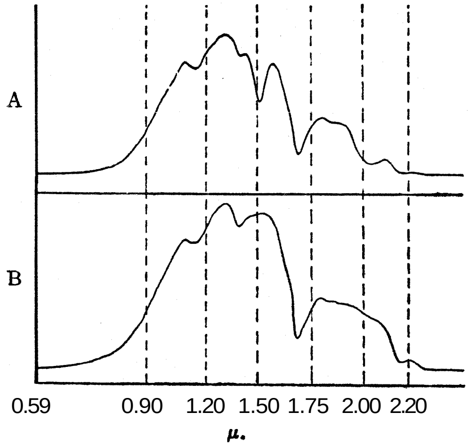

Fig. 15.—A, ethyl-α-naphthylamine, 2 mm.; B, diethyl-α-naphthylamine (purified), 2 mm.

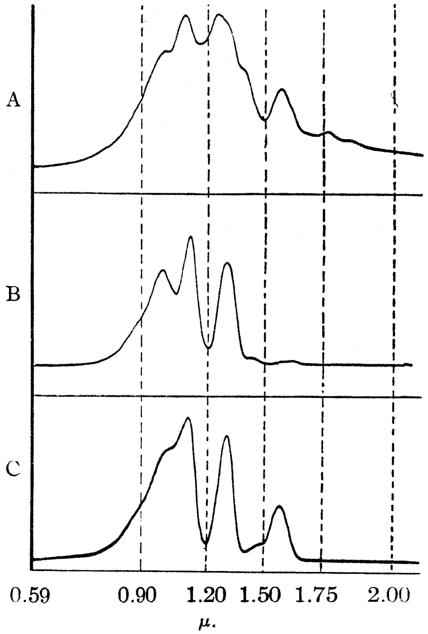

Fig. 16.—A, *p*-toluidine, 10 mm B, methyl-p-toluidine, 40 mm.; C, dimethyl-*p*-toluidine, 40 mm.

The 6.25μ N-H band may be regarded as analogous to the one at 6.9μ (6.75μ) due to C-H, while the 3.05–2.80μ, 1.55–1.49μ, 1.06–1.03μ series may parallel the 3.45μ (3.25μ) fundamental and its overtones. A combination of the 6.25μ and 3.00–3.05μ frequencies yields a wave length value of 2.03–2.05μ in good agreement with the 2.02μ value observed for the primary alkyl amines and benzylamine. This is illustrated by the following addition of the frequencies of the 6.25μ and 3.00μ values expressed in mm.$^{-1}$: 160 + 333 = 493 mm.$^{-1}$. The wave number of the observed 2.02μ band is 495 mm.$^{-1}$. The agreement is less satisfactory in the case of aniline, however, with a calculated value of 1.93μ as compared to an observed value of 2.01μ. (It will be observed that the interpretation of this band in aniline differs from that given in Part I of this paper.)

In the spectra of methyl-α- and ethyl-α-naphthylamine and methyl-p-toluidine this band occurs at 2.03μ, while in the dialkyl amines and dibenzylamine it has apparently shifted to 2.10μ.

In the region 1.21–1.23μ there seems to be evidence of a contribution to absorption by the amino group. This is shown by the records for aniline and diphenylamine in Fig. 9 and for benzyl- and dibenzylamine in Fig. 10. These values are in good agreement with the 1.20–1.24μ combination band calculated from the 6.25μ and 1.49–1.55μ maxima. There is also evidence of the existence of this band in the records for the primary and secondary alkyl amines, but the occurrence of C-H absorption at 1.20μ practically obscures it.

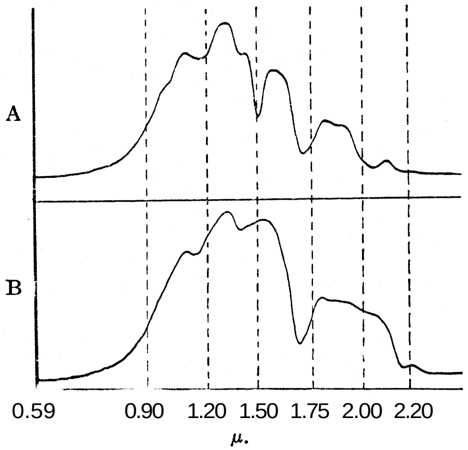

Fig. 17.—A, methyl-*p*-toluidine, 2 mm.; B, dimethyl-*p*-toluidine (purified), 2 mm.

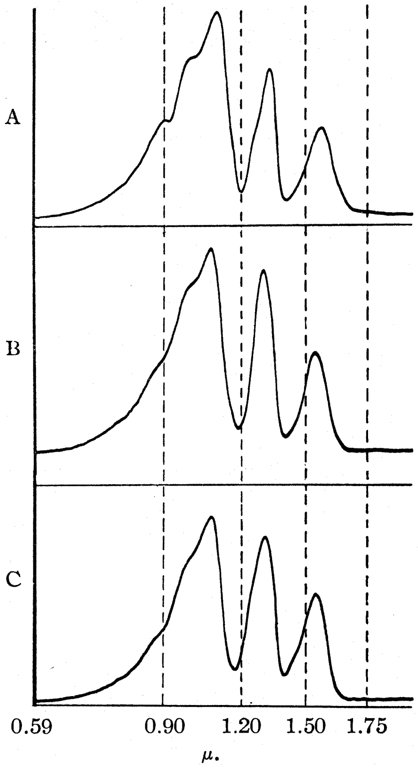

Fig. 18.—A, tri-*n*-propylamine (purified), 40 mm.; B, dimethyl-*p*-toluidine (purified), 40 mm.; C, diethyl-α-naphthylamine (purified), 40 mm.

In Table I is given a summary of the values attributed to the nitrogen-hydrogen linkage, including the measurements on mono-alkyl anilines recorded in the first portion of this paper. The values found by Bell and by Salant for the band near 3μ are included.

TABLE I

BANDS CHARACTERISTIC OF THE N H BOND

n-Propylamine	3.05,	1 . 5	1.06μ	2.02μ
Di-n-propylamine	3.05; 3.04 S[a]	1.55	1.06	2.10
n-Butylamine	3.00	1.55	1.06	2.02
Di-*n*-butylamine	3.05; 3.01 S	1.55	1.06	2.10
iso-Amylamine	3 00	1.55	1.06	2.02
Di-iso-amylamine	3.05; 3.07 S	1.54	1.06	2.10
Aniline	2.80	1.49	1.03	2.01
Diphenylamine	2.90; 2.89 S	149	1.03	[b]
Methylaniline	2 80	149	1.03	2.06
Ethylaniline	2 90	149	1.03	2.06
n-Propylaniline	2.80	1.49	1.03	[b]
n-Butylaniline	2.80	1.49	1.03	[b]
iso-Amylaniline	2.70	1.49	1.03	[b]
Benzylamine	3.00	1.55	1.06	2.02
Dibenzylamine	3.00; 3.00 S	1.55	1.06	2.10
α-Naphthylamine	2.90	1.51	1.03	[b]
Methyl-a-naphthylamine	2.90	1.51	1.03	2.03
Ethyl-a-naphthylamine	2.90	1.51	1.03	2.03
p-Toluidine	...	1.49	1.03	[b]
Methyl-p-toluidine	...	1.51	1.03	2.03

[a] All of the 3μ values are from Bell's papers, with the exception of those marked S, which are due to Salant.

[b] Records do not permit of measurement in this region.

The writer is grateful to Dr. G. R. Robertson, who purified certain of the compounds used and to Mr. W. A. Munson for assistance in obtaining the spectra recorded.

Summary

1. Using a registering spectrograph, the infra-red absorption spectra below 2.5μ have been obtained for mono-, di- and tri-n-propyl, n-butyl and iso-amylamine; mono- (aniline), di- and triphenylamine; mono-, di- and tribenzylamine; a-, methyl-a-, dimethyl-a-, ethyl-a- and diethyl-a-naphthylamine; and p-, methyl-p- and dimethyl-*p*-toluidine.

2. Bands which occur at 1.49–1.55μ and 1.03–1.06μ for the primary amines and with diminished intensities for the secondary amines but which disappear for the tertiary amines, thus apparently originating in the nitrogen-hydrogen linkages, form an "harmonic" series with a band found by Bell at 2.80–3.05μ.

3. Absorption maxima at 2.01–2.03μ and 1.21–1.23μ, apparently also characteristic of the amino group, are suggested as "combination" bands arising from the 2.80–3.05μ and 1.49–1.55μ values taken with a band found by Bell at 6.25μ.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY IN THE LABORATORIES OF PHYSIOLOGY, HARVARD MEDICAL SCHOOL]

THE DISSOCIATION CONSTANT OF ACETIC ACID AND THE ACTIVITY COEFFICIENTS OF THE IONS IN CERTAIN ACETATE SOLUTIONS[1]

BY EDWIN J. COHN, FRANCIS F. HEYROTH[2] AND MIRIAM F MENKIN

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The characterization of weak and of strong electrolytes has involved quite different conceptions and methods. The concept of partial dissociation and the method of conductivity yielded the Ostwald dilution law, and accurate constants in terms of which the dissociation of weak acids could be defined. The dissociation constant of acetic acid has been very accurately determined by this method to be 1.85×10^{-5} by Kendall.[3] Recently MacInnes[4] has shown that a slightly lower value for this constant is obtained "provided (a) that the degrees of ionization are computed in a manner which allows for inter-ionic attraction, and (b) that the resulting ion concentrations are multiplied by the appropriate activity coefficients." His values for the dissociation constant of acetic acid vary from 1.743 to 1.784×10^{-5}.

The partial neutralization of a weak acid by a strong base may also be described by the mass law. The salt of the weak acid formed by the neutralization must be considered a strong electrolyte leading to inter-ionic forces. None the less the mass law must hold provided the quantities involved are expressed as activities. When the neutralization is followed by electromotive force measurements with the hydrogen electrode the activity of the hydrogen ion is determined. The activity of the acid anion may be expressed by multiplying its stoichiometric concentration by its activity coefficient. If the activity coefficient of the acetate ion is defined by the Debye-Hückel equation, a general expression is obtained[5] which may be written in the following logarithmic form for acetic acid

$$P_{H^+} - \log\,[(CH_3COO^-)/(CH_3COOH)] = P_K - 0.5\sqrt{\mu}/(1 + \kappa b) + Ks\mu = P_{K'} \quad (1)$$

In this equation P_{H^+} and P_K are the negative logarithms respectively of the hydrogen ion activity and of the dissociation constant of the acid; μ is the ionic strength; and b and Ks and κ are the usual terms in the Debye-Hückel equation, the latter having the value of $0.33 \times 10^8\sqrt{\mu}$. The assumption made by MacInnes that the activity coefficient of the undissociated acetic acid is equal to unity has been tentatively adopted. As

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[1] A preliminary account of this investigation was communicated to the Twelfth International Physiological Congress, Stockholm, 1926, *Skandinav. Archiv*, 49 (1926).

[2] Fellow in Medicine of the National Research Council.

[3] Kendall, *J. Chem. Soc.*, *101*, 1275 (1912).

[4] MacInnes, THIS JOURNAL, 48, 2068 (1926).

[5] Cohn, *ibid.*, 49, 173 (1927).

a result K_S is attributed entirely to the acetate anion, although it includes the effect on acetic acid. This simplification influences neither the value of the apparent nor of the true dissociation constant of acetic acid.

The Dissociation Constant of Acetic Acid

The left side of Equation (1) yields the negative logarithm of the apparent dissociation constant of the acid, sometimes expressed by the symbol $P_{K'}$. At low values of the ionic strength the activity coefficient of the acetate ion approaches one and $P_{K'}$ approaches the negative logarithm of the true dissociation constant, P_K. If $P_{K'}$ is plotted as ordinate, and the square root of the ionic strength as abscissa, a graphical method of determining the true dissociation constant of the acid is obtained, for at low values of ionic strength the terms containing b and Ks become vanishingly small and linear extrapolation possible.

In the study of buffer solutions,[6,7] the useful approximation has generally been made that the concentration of the acid anion, (CH_3COO^-), could be put equal to the concentration of sodium acetate. This approximation breaks down in precisely those solutions with which we are concerned here, namely, those that are both very dilute and appreciably acid. Under these circumstances the assumption is no longer justified that the amount of the anion derived from the dissociation of the acid is negligible in comparison with that derived from the dissociation of the salt. The amount derived from the salt may be put equal to the concentration of sodium ions, and that derived from the acid to the stoichiometric concentration of hydrogen ions. The sum of these concentrations yields the concentration of the anion

$$(Na^+) + (H^+) = (CH_3COO^-) \tag{2}$$

Electromotive force measurements do not yield the stoichiometric concentration but the activity of the hydrogen ion, a_{H^+}. This quantity divided by the activity coefficient of the hydrogen ion, γ_{H^+}, yields the concentration of hydrogen ions and may be substituted in the above equation. Lewis and Randall,[8] Scatchard,[9] and Sherrill and Noyes[10] have estimated the activity coefficient of the hydrogen ion. Their results over the range employed do not differ by more than one per cent. The values employed in these calculations have been taken from a curve drawn through their values relating the activity coefficient of the hydrogen ion to the ionic strength of the solution. Taking into account the acetate

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[6] Henderson, Am. J. *Physiol.*, 15, 257 (1906); 21, 173 (1908); THIS JOURNAL, 30, 954 (1908).

[7] Washburn, *ibid.*, 30, 31 (1908).

[8] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

[9] Scatchard, THIS JOURNAL, 47, 696 (1925).

[10] Sherrill and Noyes, *ibid.*, 48, 1861 (1926).

anion derived from the dissociation of acetic acid, the complete equation for the apparent dissociation constant, $P_{K'}$, in mixtures of acetic acid and sodium acetate becomes

$$P_{H^+} - \log \frac{(Na^+) + (a_{H^+}/\gamma_{H^+})}{(CH_3COOH)} = P_K - 0.5\sqrt{\mu}/(1 + \kappa b) + K_s\mu = P_{K'} \qquad (3)$$

The concentration of acetic acid, (CH_3COOH), has been substituted for its activity and has been estimated by subtracting the concentration of the anion from the total acetate in the system.

Accurate electromotive force measurements upon dilute equimolecular mixtures of acetic acid and sodium acetate were made by Walpole[11] in 1914, and Brönsted[12] attempted certain calculations with these data in 1921. Walpole's result at very low molecular concentrations do not fall upon a straight line, probably because of the difficulty of making measurements in such dilute solutions. No attempt has been made to make measurements at these low concentrations, but from 0.02 to 0.2 M it has been possible to confirm the general trend of Walpole's data.

The determination of P_K by extrapolation becomes more accurate the lower the ionic strength of the solution. On the other hand, the usual experimental errors are encountered in measurements upon solutions of low molecular concentration. In the case of buffer mixtures this difficulty has been overcome by studying mixtures containing relatively large amounts of the weak acid but small amounts of the salt. Under these

TABLE I

ELECTROMOTIVE FORCE MEASUREMENTS UPON DILUTE ACETATE SOLUTIONS

Calculated by means of the Sørensen value of the 0.1 N calomel electrode

Total acetate M	Mole fraction of total acetate as CH_3COONa			Total acetate M	Mole fraction of total acetate as CH_3COONa		
	0.1	0.2	0.5		0.1	0.2	0.5
	Hydrogen potentials of acetate solutions				Hydrogen potentials of acetate solutions		
0.02	3.793	4.110	4.686	0.08	3.747	4.069	4.647
	3.790	4.115	4.683		3.744	4.073	4.650
	3.788	4.116	4.686		...	4.074	4.643
	3.793	4.110	4.690		...	4.070	4.646
	3.794	4.115	4.691		...	4.070	4.650
	3.787	4.119	4.692		...	...	4.644
	3.791	4.114	4.688		3.746	4.071	4.647
0.04	3.770	4.091	4.666	0.20	3.708	4.037	4.623
	3.770	4.091	4.662		3.710	4.039	4.622
	.	4.090	4.665		3.717	4.036	4.623
		4.088	4.672		3.712	4.041	4.618
		4.092	4.672		3.708	4.043	4.623
	...	4.093	4.676		3.706	4.044	4.621
	3.770	4.091	4.669		3.710	4.040	4.621

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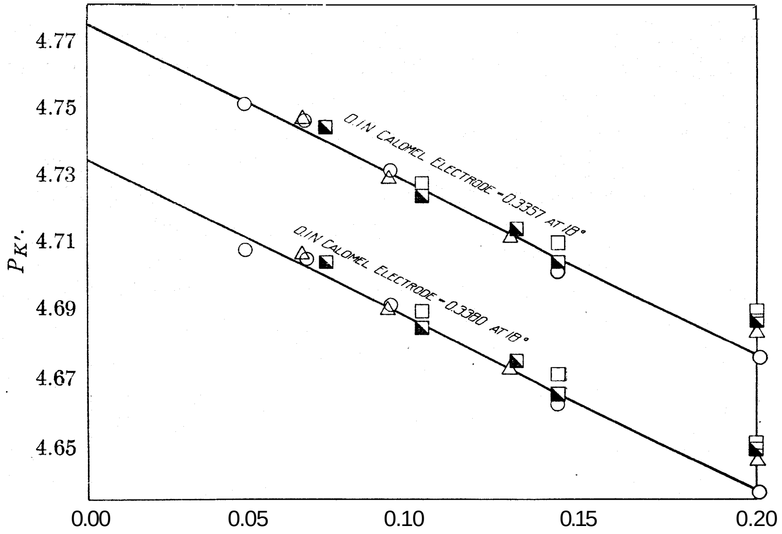
[11] Walpole, J. *Chem. Soc.*, 105, 2501, 2521 (1914).

[12] Bronsted, *ibid.* **119,** 574 (1921).

circumstances the molecular concentration may be retained at a relatively high level and the ionic strength allowed to reach a much lower value. Measurements have now been made upon solutions containing four and nine times as much acetic acid as sodium acetate. A 0.02 molecular solution of acetic acid of which only 0.1 has been transformed into sodium acetate has an ionic strength of 0.00217. None the less this solution is well buffered and readily studied by means of the hydrogen electrode. Measurements upon such solutions are recorded in Table I and, together with Walpole's measurements, graphically represented in Fig. 1.



Square root of ionic strength.

Mole fractions of CH_3COONa: ○, 0.1; △, 0.2; ▣, 0.5; ◪, Walpole, 0.5.

Fig. 1.

Measurements upon dilute acetic acid solutions have been reported by Loomis and Acree[13] and Walpole. Their results are not in entire agreement, and the empirical dilution law deduced by Walpole from his data is at variance with the theoretical equation under consideration. These data upon dilute solutions of acetic acid, like those upon extremely dilute buffer solutions, show an apparent change in $P_{K'}$ upon dilution far greater than should be expected. For the present it seemed desirable to restrict the investigation to buffered solutions whose concentrations were not lower than 0.01 molar.

The electromotive force measurements that have been made have been calculated as hydrogen potentials by means of Sørensen's[14] value for the 0.1 N calomel electrode in order to render them comparable to Walpole's

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[13] Loomis and Acree, *Am. Chem. J.*, 46, 585 (1911).

[14] Sørensen, *Compt. rend. trav. lab. Carlsberg*, *8*, *1* (1909).

measurements upon standard acetate solutions. Walpole states that his measurements were constant and reproducible to 0.1 millivolt. He attempted to correct for diffusion potentials by the Bjerrum extrapolation method but reported no diffusion potential as great as 0.1 millivolt for the solutions considered in Table I. He noted the extremely small diffusion potentials of all of the acetate solutions that he studied. In our measurements the saturated potassium chloride salt bridge was employed and no correction for diffusion potentials attempted.

The mean values of the hydrogen potentials recorded in Table I have been employed in Table II for the calculation of the apparent dissociation constant of acetic acid by means of Equation (3). The measurements upon equimolecular mixtures of acetic acid and sodium acetate of Walpole and of Michaelis and his collaborators[15] are included in Table II. Our results and those of Walpole upon solutions with ionic strengths less than 0.05 (excepting those of Walpole upon the most dilute solutions, which are given in parentheses) are graphically represented in Fig. 1, in which $P_{K'}$ is the ordinate and the square root of the ionic strength the abscissa.

In dilute solutions, which alone are considered in Fig. 1, the change in $P_{K'}$ is nearly proportional to the square root of the ionic strength. Under these circumstances the values of the apparent dissociation constant, calculated in Table II, may be employed in estimating the true dissociation constant of acetic acid. This was attempted by the graphical extrapolation in Fig. 1. A straight line originating at P_K 4.733 (where $\sqrt{\mu} = 0$) has been drawn with the theoretical slope of 0.5 demanded by the Debye equation. This line passes between the lower set of experimental points, but the specific ion effects, which are known to occur from the study of more concentrated solutions, and are evident in the figure when $\sqrt{\mu}$ is greater than 0.1, exert a slight influence even in more dilute solution. Were these effects considered, a slightly lower value of P_K would have to be adopted, approximately equal to 4.73. The value of P_K, 4.733, equal to $Ka = 1.85 \times 10^{-5}$, is identical with Kendall's estimate of the dissociation constant of acetic acid derived from conductivity measurements. The uncertainty in obtaining a value of P_K from the extrapolation of the electromotive force measurements in Fig. 1 is not greater than $\doteq$ 0.005. The results of Kendall's conductivity measurements and these electromotive force measurements are thus entirely consistent with each other, provided Sørensen's value of the 0.1 normal calomel electrode is employed.

The Value of the 0.1 N Calomel Electrode

The value of the 0.1 N calomel electrode has long been in doubt by over 2 millivolts. As a result the entire scale upon which so much chemical and

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[15] Michaelis and Krüger, *Biochem. Z.*, 119, 307 (1921); Michaelis and Kakinuma, *ibid.*, 141, 394 (1923).

TABLE II

THE APPARENT DISSOCIATION CONSTANT OF ACETIC ACID IN DILUTE ACETATE SOLUTIONS

Calculated by means of the Sørensen value of the 0.1 *N* calomel electrode

Total acetate	P_{H^+}	(Na^+)	(H^+)	(CH_3COOH^-)	$\sqrt{\mu}$	$\log \frac{(CH_3COOH)}{(CH_3COO^-)}$	$P_{K'}$
Mole fraction of total acetate as CH_3COONa = 0.1							
0.020	3.791	0.002	0.000170	0.002170	0.0466	0.915	4.706
.040	3 770	.004	,000181	.004181	.0647	933	4.703
.080	3.746	.008	.000194	.008194	.0905	943	4.689
.200	3.710	.020	.000220	.020220	.142	.949	4.659
.400	3.681	.040	,000239	.040239	.201	.951	4.632
1.000	3641	.100	,000272	.100272	.317	.953	4.594
Mole fraction of total acetate as CH_3COONa = 0 2							
0.020	4.114	0.004	0000082	0.004082	0.0639	0.591	4.705
.040	4.091	.008	,000087	.008087	.0899	.597	4.688
.080	4.071	.016	.000094	.016094	.1269	.599	4.670
.200	4.040	.040	.000105	.040105	,2003	.601	4.641
.400	4.020	.080	.000113	08011.7	.283	.601	4.621
Mole fraction of total acetate as CH_3COONa = 0.5							
0.020	4.688	0.010	0.000023	0.010023	0.100	$\bar{1}$.998	4.686
.040	4.669	.020	.000023	,020023	142	$\bar{1}$.999	4.668
.080	4.647	.040	.000026	,040026	.200	.OW	4.647
.200	4.621	.100	.000029	.100029	317	.000	4.621
Walpole's measurements							
0.002	4.758	0.001	0.000017	0.001017	0 0319	$\bar{1}$.985	(4.743)
.004	4.736	.002	.000019	.002019	.0449	$\bar{1}$.992	(4.728)
.010	4.706	.005	.000021	005021	.0709	$\bar{1}$ 996	4.702
.020	4.684	.010	000023	.010023	.100	$\bar{1}$.998	4.682
.032	4.673	.016	.000023	.016023	.129	$\bar{1}$.999	4.672
.040	4.663	,020	,000025	,020025	.142	$\bar{1}$.999	4.662
.080	4.645	.040	.000026	040026	.200	.000	4.645
.200	4.623	.100	.000029	100029	.317	.000	4.623
.400	4.606	.200	.000030	.200030	.447	.000	4.606
Michaelis and Kriiger's measurements							
0,200	4.616	0.100	0.000029	0.100029	0.317	0.000	4.616
Michaelis and Kakinuma's measurements[16]							
0.010	4695	0.005	0.000021	0.005021	0.0709	$\bar{1}$.996	4.691
.200	4 607	.100	000029	.100029	.317	.000	4.607

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[16] Dr. Michaelis has made the following personal communication to me regarding the **PH** of standard acetate as calculated by Michaelis and Kakinuma: "The activity coefficients of HCl had been calculated by Lewis and Randall from the mean activity of HCl. In order to obtain the activity coefficient of the hydrogen ion one had to apply the hypothesis that $\gamma_{H^+} = \gamma_{Cl^-} = \sqrt{\gamma_{HCl}}$. Such an assumption, **which** is certainly justified for molecules such as KCl, is not true for HCl. It seemed to me better to take γ_{H^+} in $N/500$ HCl = 1. Upon this assumption the value P_H 4.607 was obtained. In the meantime, γ_{H^+} has been determined more carefully by Scatchard, and we should take γ_{H^+} for 0 002 HCl = 0.956. In this case the value 4.607 must be changed to 4.627, **which** is in agreement with Walpole's original value, my own earlier values, and Cohn's new measurements."

biochemical work depends is in doubt. Sørensen's value for the 0.1 *N* calomel electrode at 18° was 0.3380, and Clark[17] has calculated a value for this half cell of 0.3360 from Lewis, Brighton and Sebastian's[18] measurements upon the normal calomel electrode at 25°. Although he has pointed out this discrepancy, Clark has suggested that the Sørensen value for the 0.1 N calomel electrode be retained, since so much work already published depends upon it.

In certain incidental measurements of the activity coefficients of the hydrogen ion in dilute hydrochloric acid solutions, we were forced to the use of the Lewis, Brighton and Sebastian value for the 0.1 N calomel electrode.[19] The Sørensen value rendered the accumulated data uninterpretable. Sørensen's measurements were made in 1909, and his value depended upon estimates of dissociation derived from conductivity data. He has recently pointed out, in collaboration with Linderstrøm-Lang,[20] that the value 0.3357 is obtained provided the activity of the hydrogen ion is referred to. They have suggested retaining both the old and the new value, the one referring to the concentration, the other to the activity of hydrogen ions. Scatchard[8] has also recalculated Sørensen's old value "using 0.0801 instead of 0.0917 for the mean activity of the ions of 0.1 M hydrochloric acid." "Taking 0.0762 for the activity of the chloride ion in 0.1 M potassium chloride" Scatchard obtains 0.3353 for the half cell at 25°. The same temperature coefficient as has been previously employed renders Scatchard's estimate identical with Sørensen's own revision of this electrode potential, 0.3357 at 18°. Lewis and Randall in recalculating the result of Lewis, Brighton and Sebastian estimate "the activity of chloride ion in 0.1 M KCl . . . . to be 0.0794, whence for the deci-normal electrode . . . . E = –0.3351" at 25°. Their value for the half cell thus becomes 0.3355 at 18°.

These various estimates of the 0.1 N calomel electrode based upon the activity of hydrogen ions in 0.1 N solution thus vary from 0.3355 to 0.3360 at 18°. If the electromotive force measurements reported are calculated by means of these values of the 0.1 N calomel electrode, the value of P_K becomes greater than that estimated by means of Sørensen's original value. The upper set of points in Fig. 1 has been calculated on the basis of the value 0.3357 for the 0.1 N calomel electrode at 18°. Besides increasing all the values of $P_{K'}$ by approximately 0.04, this effects a relatively greater change in $P_{K'}$ the more acid the reaction. For this reason measurements made upon mixtures containing but a small proportion of sodium acetate are raised in $P_{K'}$ more than are equimolecular mixtures by the assumption

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[17] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Company, Baltimore, Md., 1922.

[18] Lewis, Brighton and Sebastian, THIS JOURNAL, 39,2245 (1917).

[19] Cohn and Berggren, *J. Gen. Physiol.*, 7, 45 (1924).

[20] Sørensen and Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, 1 (1924).

of a lower value for the calomel electrode. The points representing the measurements upon the most dilute acid solutions appear to fall more nearly on a straight line when calculated by means of the lower value for the calomel electrode.

A far greater uncertainty is introduced in the interpretation of these measurements by the value ascribed to the calomel electrode than by the measurements themselves. The uncertainty regarding the calomel electrode depends upon the activity coefficient of the hydrogen ion in cells containing strong electrolytes in concentrations as great as 0.1 molal. The inter-ionic forces in such solutions are appreciable. Electromotive force measurements by means of the hydrogen electrode can, however, be carried on upon mixtures of a weak acid and its salt in solutions of relatively high molecular concentration, but of such low ionic strength that specific ion effects can practically be neglected. It is therefore suggested that electromotive force measurements upon mixtures of a weak acid and its salt might be used in the standardization of calomel electrodes (see also the papers of Michaelis and his collaborators[15]) since the dissociation constants obtained by the extrapolation of such data may be compared with the very accurate constants of the weak acids yielded by means of the Ostwald dilution law and conductivity measurements.

In the recalculation of the dissociation constants of weak acids recently reported by MacInnes, "the only case in which there is a definite trend in the value of the constant K is that of acetic acid in which there is a change of 2.2% from 0.07 to 0.002 *N*. This is probably due to the fact that the conductance data for the acid and its sodium salt were obtained by different workers." This is unfortunate and renders it desirable either that new conductance work be done on acetates, or that electromotive force measurements be made upon the other weak acids studied by MacInnes and by Sherrill and Noyes. The values calculated by MacInnes range in P_K from 4.749 to 4.759. The difference of 0.01 in P_K or P_{H^+} is greater than the probable error in the measurements reported, but only one-fourth as large as the difference introduced by the use of the new and the old values of the 0.1 N calomel electrode. If MacInnes' calculations are assumed to yield the correct value of P_K, the value of the 0.1 N calomel electrode should lie between 0.3364 and 0.3370.

It is not possible, at this time to do more than indicate the interdependence of estimates of the dissociation constant of a weak acid derived from conductivity measurements, with those derived from electromotive force measurements and with the value of the calomel electrode. A redetermination of any of these quantities will yield more accurate values of all the others. The values of the negative logarithm of the dissociation constant of acetic acid, P_K, derived from the reported electromotive force measurements upon acetate solutions, and the various values of the 0.1 N calomel electrode are reported in Table III, and compared with the values of P_K derived from conductivity measurements by Kendall and MacInnes.

TABLE III

THE RELATION BETWEEN THE VALUES OF THE DISSOCIATION CONSTANT OF ACETIC ACID AND OR THE 0.1 N CALOMEL ELECTRODE

	Values of the 0.1 *N* calomel electrode at 18°	Values of P_K denved from elertromotive force measurements	Values of P_K derived from conductivity measurements	
Sørensen[14]	0.3380	4.730	Kendall[3]	4.733
Clark[17] from Lewis, Brighton and Sebastian's measurements	.3360	4.765		...
Sørensen and Linderstrøm-Lang[20]	.3357	4.770	MacInnes[4]	4.749 to 4.759
Scatchard[9] from Sørensen's measurements	.3357	4.770		
Lewis and Randall[8]	.3355	4.773		...

The Activity Coefficients of the Ions in Certain Acetate Solutions

The activity coefficients of the acetate anion that may be derived from electromotive force measurements are independent of the value ascribed to the calomel electrode. The difference between $P_{K'}$ in any given solution and P_K yields the negative logarithm of the activity coefficient of the anion in that solution, provided both are calculated by means of the same value for the reference electrode. In Fig. 1 values of $P_{K'}$, derived from hydrogen electrode measurements upon dilute mixtures of acetic acid and sodium acetate, were plotted against $\sqrt{\mu}$, and graphical extrapolation yielded a value of P_K equal to 4.733, with an uncertainty not greater than 0.005. A slightly lower value of P_K, perhaps 4.730, would have resulted had not linear extrapolation been entirely relied upon, for the effect of the size of the ions, which becomes so significant a factor in more concentrated solutions, cannot be entirely neglected in these dilute solutions.

Taking the round value 4.73 for P_K the values of the constants in Equation (3) have been estimated from measurements of the PH of systems containing known amounts of acetic acid and sodium acetate, and therefore having known ionic strengths. The ionic strength per liter of solution rather than per thousand *g.* of water is always given. Measurements of the PH of the same mixture of acetic acid and sodium acetate, at various dilutions, may be employed, and values of b and *Ks* deduced from them by means of Equation (3). If, on the other hand, values of b and Ks, derived from such calculations, be assumed, the equations can be solved for P_K. In this way the experimental results can be considered from the point of view of the additional information that they yield regarding the dissociation constant of acetic acid.

The stock solutions employed in preparing the acetate mixtures consisted of 4 *M* sodium hydroxide and of 4 *M* and 8 *M* acetic acid. The acetic acid solutions were regularly standardized against the sodium hydroxide and these in turn were standardized against 0.1 *M* oxalic acid. The stock solutions were always diluted approximately to 0.1 *M* for standardization.

The solutions to be measured were prepared by placing a given amount of acetate as acetic acid in a volumetric flask and transforming the desired amount into sodium acetate by the addition of sodium hydroxide. Boiled distilled water was then added to bring the solution to volume. At least two, and sometimes three, mixtures of each mole fraction, at each concentration, were measured by means of three different electrodes. The electromotive force measurements upon dilute acid solutions are reported in Table I and have already been considered with respect to certain of the implications to be derived from them. These solutions varied in molecular

TABLE IV

ELECTROMOTIVE FORCE MEASUREMENTS UPON CONCENTRATED ACETATE SOLUTIONS

Calculated by means of the Sørensen value of the 0.1 *N* calomel electrode

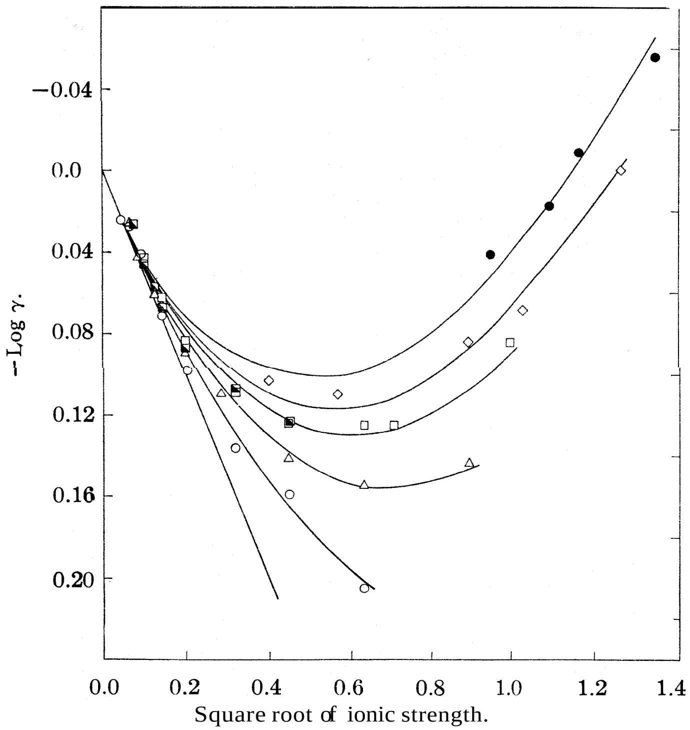
Total acetate	Mole fraction of total acetate as CH_3COONa				
	0.1	0.2	0.5	0.8	0.9.
M	Hydrogen potentials of acetate solutions				
	(Walpole's Measurements)				
0.20	3 723	4.047	4.626	5.227	5.574
	(New Measurements)				
0.40	3.686	4.019	4.616	5.219	...
	3.691	4.016	4.609	5.220	...
	3.680	4.021	4.608	5.220	...
	3.677	4.021	4.605	5.226	...
	3.676	4.025	4.611	5.233	...
	3.677	..	4.605	5.217	..
	3.681	4.020	4.609	5.222	...
0.80	...	...	4.607	...	...
	...	...	4.605	...	...
	...	...	4.604	...	...
	...	...	4.605	...	...
1.00	3.643	3.986	4.608	5.251	5.645
	3.646	3.983	4.610	5.243	5.642
	3.642	3.981	4.602	5.248	5.644
	3.636	3.991	4.602	5.253	5.643
	3.641	3.991	4.605	5.251	5.638
	3.637	3.989	4.602	6.245	5.646
	3.641	3.987	4.605	5.248	5.643
1.33	...	...	...	5.265	5.663
	...	...	...	5.262	5.666
	...	...	...	...	5.671
	...	...	...	5.263	5.667
1.50	...	...	...	...	5.697
	...	...	...	...	5.694
	...	...	...	...	5.696
	...	...	...	...	5.682
	...	...	...	...	5.694
	...	...	...	...	5.693
2.00	3.621	3.973	4.642	5.329	5.736
	3.622	3.972	4.648	5.334	5.728
	3.611	3.973	4.650	5.328	5.742
	3.617	3.975	4.643	5.340	5.749
	3.617	3.977	4.647	5.338	5.738
	3.615	...	4.647	5.326	5.745
	3.617	3.974	4.646	5.332	5.740
4.00	3.572	3.985	...	...	...
	3.572	3.981	...	...	...
	3.569	3.980	...	...	...
	...	3.988	...	...	...
	...	3.990	...	...	...
	3.571	3.985	...	...	...

concentration from 0.02 to 0.2, and in ionic strength from 0.00216 to 0.1. This range is extended by the data in Table IV, in which are reported measurements upon solutions more concentrated than those studied by Walpole. The concentrations varied from 0.2 to 4.0 molecular, and the mole fraction of total acetate as CH_3COONa from 0.1 to 0.9. The ionic strengths in Table IV thus vary from 0.02016 to 1.80. If all of the measurements be considered they range in ionic strength from 0.00216 to 1.80.

The averages are taken in Table IV of the different electromotive force measurements made upon these different acetate solutions. With a few exceptions each solution was prepared several times, from different stock solutions, and studied by more than one of us. In Table V, $P_{K'}$ has been calculated from the average PH measurements by means of Equation (3). In the accompanying figure $-\log \gamma$ has been plotted as ordinate and the square root of the ionic strength as abscissa. The straight line which represents the limiting slope for a univalent ion originates at $P_K = 4.73$, and the values of $-\log \gamma$, given as ordinates, are calculated on this basis. The curves which pass through the experimental points have been constructed on the basis of the values of b given in Table V. The term Ks has been retained constant at 0.16 throughout these preliminary calculations. It is probable that certain of the measurements could have been more accurately represented by varying not only b but Ks as well. This was certainly the case with the most alkaline series studied. However, it was not believed that this was warranted by the experimental accuracy that has been achieved, and the simplification in calculation that results renders it desirable to consider Ks constant.

The description of these measurements upon diverse mixtures by means of a constant value for the salting-out constant is noteworthy. In the study of the activity coefficients of the ions in certain phosphate solutions, it was found possible to describe the data on the basis of a constant value for b, but a variable value for Ks. It was pointed out that this approximation could be justified only in so far as the Debye-Hückel equation was being employed as an empirical interpolation formula. Though the same reservation must be made in connection with the present investigation, it should be pointed out that in this case we are not dealing with the univalent and bivalent salts of a weak acid but with the weak acid itself and its univalent salt. Under these circumstances not only is the change of the activity coefficient with concentration very much less—the limiting slope being 0.5 instead of 1.5—but in all save the most dilute acid solutions the ionic strength is proportional to the sodium ion. Whether or not this simple proportionality results in the apparent constancy of Ks must await further experimentation. It may well be a real rather than an apparent phenomenon, to be expected in other comparable mixtures of weak univalent acids and their salts.

Another method of considering these data is presented in Table V. The values of b and *Ks* employed in the construction of the curves in Fig. 2 have been used in the calculation of the values of $-\log \gamma$ given in the table. These values of the negative logarithm of the activity coefficient of the acetate anion, added to the negative logarithm of the apparent dissociation constant $P_{K'}$, yield in the last column calculated estimates of the negative logarithm of the true dissociation constant, P_K. Errors either in the theoretical calculation of the activity coefficient or in the experimental determination of the PH appear as deviations from the theoretical value of this constant. The method of calculation has the further advantage that these deviations are proportional to their value as errors in PH. It will be noted that in all of the calculated values of P_K, made from measurements of the PH of solutions varying in mole fraction of sodium acetate from 0.1 to 0.9 and in ionic strength from 0.00217 to 1.80, none is higher than 4.741 and none lower than 4.721. Within the range that has been considered, no error in estimating the PH of a solution greater than 0.02



Mole fraction of CH_3COONa: ○, 0.1; △, 0.2; □, 0.5; ◇, 0.8; ●, 0.9; ◪, Walpole, 0.5.

Fig. 2.

TABLE V

A COMPARISON OF THE CALCULATION AND THE MEASUREMENT OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF CH_3COOH AND CH_3COONa

Mole fraction of total acetate as CH_3COONa	Total acetate concentration M	Ionic strength μ	$p_{K'}$, obs.[a]	$-\log\gamma$, obs. $4.73-p_{K'}$	$-\log\gamma$,[b] calcd.	p_K, calcd[a] $p_{K'}+\log r$[b]
0.1	0.02	0.00217	4.706	0.024	0.023	4.729
	.04	.00418	4.703	.027	.030	4.733
	.08	.00819	4.689	.041	.043	4.732
	.20	.02022	4.666	.064	.065	4.731
	.40	.04024	4.632	.098	.089	4.721
	1.00	.10027	4.594	.136	.129	4.723
	2.00	.20000	4.571	.159	.165	4.736
	4.00	.40000	4.525	.205	.201	4.726
0.2	0.02	0.0041	4.705	0.025	0.029	4.734
	.04	.0081	4.688	.042	.041	4.729
	.08	.0161	4.670	.060	.055	4.725
	.20	.0401	4.645	.085	.081	4.726
	.40	.0801	4.621	.109	.105	4.726
	1.00	.2000	4.589	.141	.138	4.727
	2.00	.4000	4.576	.154	.155	4.731
	4.00	.8000	4.587	.143	.147	4.734
0.5	0.02	0.010	4.686	0.044	0.044	4.730
	.04	.020	4.668	.062	.059	4.727
	.08	.040	4.647	.083	.077	4.724
	.20	.100	4.624	.106	.104	4.728
	.40	.200	4.609	.121	.123	4.732
	.80	.400	4.605	.125	.130	4.735
	1.00	.500	4.605	.125	.127	4.732
	2.00	1.000	4.646	.084	.090	4.736
0.8	0.20	0.160	4.625	0.105	0.109	4.734
	.40	.320	4.620	.110	.117	4.737
	1.00	.800	4.646	.OM	.088	4.734
	1.33	1.067	4.661	.069	.060	4.721
	2.00	1.600	4.730	.000	− .005	4.725
0.9	0.20	0.18	4.620	0.110	0.101	4.721
	1.00	.90	4.689	.041	.052	4.741
	1.33	1.20	4.713	.017	.015	4.728
	1.50	1.35	4.739	− .009	− .004	4.735
	2.00	1.80	4.786	− .056	− .065	4.721
					Average	4.720

[a] Calculated on the basis of the value 0.3380 for the 0.1 N calomel electrode at 18°. The values at 0.2 M are the averages of those obtained by Walpole and by us.

[b] The values of $-\log\gamma$ have been calculated by means of the equation

$$\left(\frac{0.5\sqrt{\mu}}{1+\kappa b}-0.16\mu\right)$$

The following values of 0.33×10^8 b were employed for the mole fractions of total acetate as the sodium salt from 0.1 to 0.9: 0.3, 0.7, 1.0, 1.2, 1.5.

should therefore be expected in employing the values for b and K_S that have been deduced from these data.

Moreover, the average of all of these calculated values of P_K is 4.729, which is in excellent agreement with the value obtained by graphical extrapolation in Fig. 1. In so far as the Sørensen value is accepted for the 0.1 N calomel electrode, it therefore appears that 4.73 may be employed as the negative logarithm of the dissociation constant of acetic acid; Ka = 1.86×10^{-5}. This result, as we have seen, is in excellent agreement with Kendall's value of 1.85×10^{-5}, an estimate based upon conductivity data uncorrected for inter-ionic forces. Recalculation of the data in Table V by means of the value 0.3357 for the 0.1 N calomel electrode yields a value of P_K higher by approximately 0.04. The activity coefficients of the acetate anion that have been estimated appear to be calculable, regardless of any assumption regarding the calomel electrode, by means of the Debye-Hückel equation and the appropriate constants.

The acetate solutions that have generally been used as standard buffers are those studied by Walpole and by Michaelis and his collaborators. Their measurements were, for the most part, upon solutions whose total acetate concentration was 0.2 M. These solutions are sufficiently dilute and all but the most acid are of so nearly the same ionic strength that the apparent dissociation constants calculated from the PH measurements only vary from 4.615 to 4.689. This constancy unquestionably demonstrates why it was possible to apply the mass law to the titration of univalent weak acids by strong bases without considering the activity coefficients of the anions.[6,15,17] Indeed, in the most diverse solutions that have now been studied $P_{K'}$ varies only from 4.52 to 4.79. As a first approximation there can be no doubt, therefore, that the dilution of acetate buffer solutions does not greatly affect their acidity.

The electromotive force measurements made by Walpole upon the titration of 0.2 M acetic acid by means of sodium hydroxide have been employed in Table VI in the calculation of $P_{K'}$ on the basis of both the old and the new values of the 0.1 N calomel electrode. The former have been subtracted from 4.73, and the latter from 4.77 to yield estimates of $-\log \gamma$, given in the fourth and fifth columns.

The complete Debye-Hückel equation that has been employed in the more concentrated acetate mixtures that have now been studied is not necessary for the characterization of the dilute acetate mixtures studied by Walpole and previous investigators. As has previously been pointed out,[1] the changes in the apparent dissociation constant of such solutions can be satisfactorily calculated by omitting the salting-out term in the Debye-Hückel equation and employing instead so high a value for b as 5.4×10^{-8} cm. Values of $-\log \gamma$, calculated by this approximation, are compared with those previously deduced for concentrated solutions in the

TABLE VI

RECALCULATION OF WALPOLE'S ELECTROMOTIVE FORCE MEASUREMENTS UPON THE NEUTRALIZATION OF 0.2 MOLAL ACETIC ACID BY SODIUM HYDROXIDE AT 18°

Mole fraction of total acetate as CH_3COONa	P_K' 0.1 N electrode = 0.3380[a]	P_K'', 0.1 N electrode = 0.3357[a]	$-\text{Log } \gamma$, $4.73 - P_K'$	$-\text{Log } \gamma$, $4\ 77 - P_K''$	$-\text{Log } \gamma$, calcd. $\left(\frac{0.5\sqrt{\mu}}{1 + 1.8\sqrt{\mu}}\right)$	$-\text{Log } \gamma$, calcd., $\left(\frac{0.5\sqrt{\mu}}{1 + \kappa b} - 0.16\mu\right)$
0.000	4.665	4.744	0.065	0.026	0.021	...
.005	4.676	4.743	.054	.027	.023	...
.010	4.689	4.744	.041	.026	.026	...
.015	4.676	4.729	.054	.041	.029	...
.020	4.683	4.729	.047	.041	.031	...
.025	4.675	4.720	.055	.050	.033	...
.030	4.664	4.709	.066	.061	.036	...
.040	4.667	4.709	.063	.061	.040	...
.050	4.676	4.718	.054	.052	.043	...
.075	4.674	4.716	,056	.054	051	...
.100	4.672	4.713	.058	.057	.057	0.065
.200	4.648	4.688	.082	.082	.074	.082
.300	4.637	4.677	.093	.093	.085	.092
.400	4.630	4 670	.100	.100	.094	.099
.500	4.626	4.666	.104	.104	.101	.105
.600	4.626	4.666	.104	.104	.107	.108
,700	4.623	4.663	.107	.107	.112	.109
.750	4.615	4.655	.115	.115	.114	.110
.800	4.625	4.665	.105	.105	.116	.109
.850	4.620	4.660	.110	.110	.118	.105
.900	4.619	4.659	.111	.111	.120	.101
.950	4.615	4.655	.115	.115	.122	...
.962	4.615	4.655	.115	.115	.123	...
.975	4.619	4.659	.111	.111	.123	...
.987	4.622	4.662	.108	.108	.123	...

[a] Walpole's results were calculated by means of the value 0.0577 for RT/F at 18°. We have recalculated his results with the same value though the other measurements in this paper have been calculated with the value 0.05772

final columns of Table VI. Until 0.8 of the acetic acid has been transformed into the sodium salt, the two equations yield results which agree within 0.01 PH. In more alkaline solutions the approximation equation yields too high results since the salting-out phenomenon is encountered there. The agreement with the values of the activity coefficients calculated from Walpole's data by means of the old value of the 0.1 N calomel electrode, and the value 4.73 for P_K, is adequately represented by either of the interpolation equations from mole fraction 0.1 to 0.9. These successive approximations render it possible to estimate the activity coefficients and therefore the ***PH*** of these solutions with an error not greater than 0.01 in ***PH***. The general relations that have been deduced thus include and are capable of characterizing the solutions studied by Walpole.

In the more acid solutions studied by Walpole the values of $-\log \gamma$ calculated by means of the value 0.3380 for the 0.1 *N* calomel electrode diverge widely from what should be expected from the Debye equation. Indeed the values of $-\log \gamma$ calculated in Table VI show no significant drift from acetic acid to the mixture containing 0.1 mole fraction sodium acetate, although $\sqrt{\mu}$ varies from 0.046 to 0.142 and the calculated values of $-\log \gamma$ from 0.021 to 0.057. If, however, the value 0.3357 is employed for the 0.1 *N* calomel electrode and 4.77 for the negative logarithm of the dissociation constant of

TABLE VII

INTERPOLATED VALUES OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF CH_3COOH AND CH_3COONa

Concn. of total acetate, *M*	Mole fraction of total acetate as CH_3COONa								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	$-\log \gamma = 0.5\sqrt{\mu}/(1 + \kappa b) - 0.16\mu$								
0.05	0.034	0.045	0.053	0.060	0.064	0.069	0.071	0.075	0.073
.10	.047	.062	.071	.078	.084	.088	.091	.093	.089
.20	,065	.082	.092	.099	.105	.108	.109	.109	.101
.40	.088	,106	.115	.119	.123	.123	.120	.118	.100
.60	.105	,120	.127	.130	.129	.125	.119	.112	.089
.80	.118	.130	.136	.134	1 3	.123	.112	.102	.072
1.oo	.129	.139	.140	.134	.127	.117	.102	.088	.052
1.20	.138	.144	.141	.133	.123	.109	.090	.071	.030
1.40	.146	.148	.143	.130	.116	.099	.075	.054	.007
1.60	.153	.152	.142	.126	.108	.086	.061	.035	− .016
1.80	.159	.153	,142	,121	.100	.075	.044	.016	− .040
2.00	.166	.155	.139	.115	.090	.061	.028	− .005	− .065

TABLE VIII

INTERPOLATED VALUES OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF CH_3COOH AND CH_3COONa

Ionic strength of acetate soln., μ	Mole fraction of total acetate as CH_3COONa								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	$-\log \gamma = 0.5\sqrt{\mu}/(1 + \kappa b) - 0.16\mu$								
0.02	0.065	.0061	0.061	0.060	0.059	0.059	0.058	0.058	0.056
.04	.088	.082	.080	.078	.077	.077	.075	.075	.071
.06	.105	.095	.092	.090	.089	.088	.086	.085	.080
.08	.118	.106	.102	.099	.098	.096	.094	.093	.087
.10	.129	.114	.110	.106	.105	.103	.101	.099	.092
.12	.138	.120	.115	.112	.110	.108	.105	.103	.095
.14	.146	.126	.120	.116	.114	.112	.109	.107	.098
.16	.153	.130	.124	.119	.117	.114	.111	.109	.099
.18	.159	.134	.127	.123	.120	.117	.114	.111	.101
20	.166	.139	.131	.126	.123	.120	.116	.114	.102
.40	.202	.155	.142	.134	.130	.125	.120	.116	.098
.60	...	.155	.139	.128	.123	.117	.110	.105	.083
.80	...	.147	.127	.115	.108	.101	.093	.088	.063
1.oo	...	...	...	...	.090	.083	.074	.067	.040
1.20	...	...	...	...	...	...	...	.045	.015
1.40	...	...	...	...	...	...	...	.021	− .011
1.60	...	...	...	...	...	...	...	− .005	− .038
1.80	...	...	...	...	...	...	...	...	− .065

acetic acid this discrepancy is largely removed. Walpole's results and those that are now reported are rendered more consistent by the use of what must now be considered, upon other grounds, a more probable value for the 0.1 N calomel electrode.

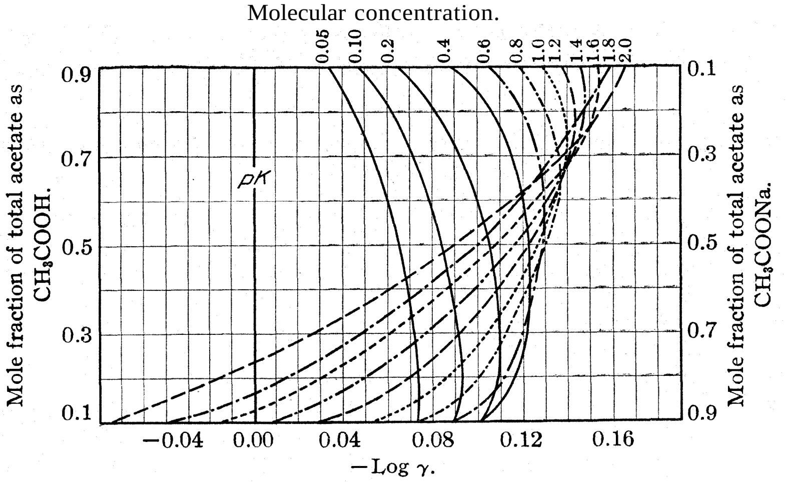


Fig. 3.

It has become a matter of convenience in a great deal of chemical and biochemical work to prepare solutions of known P_H and ionic

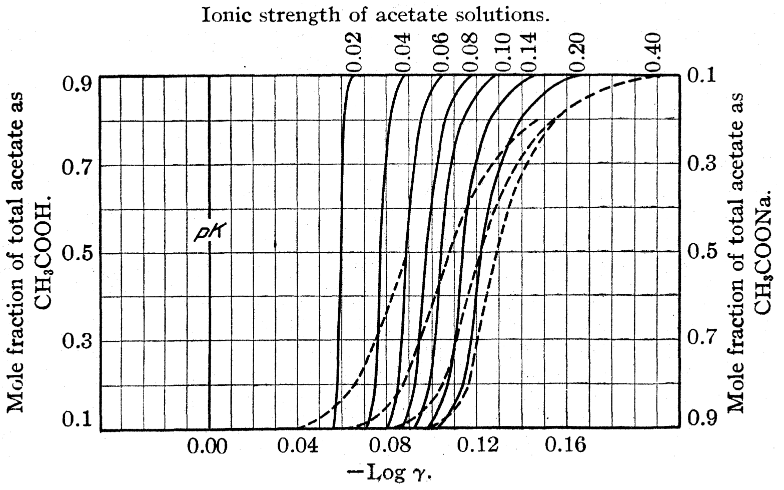


Fig. 4.

strength, and the present paper is a contribution to this end. It therefore seemed desirable to construct interpolation tables so as to facilitate the preparation of any desired solution of known P_H and ionic strength.

This has been done by calculating values of $-\log \gamma$ for different mixtures of acetic acid and sodium acetate for even values of the total acetate concentration (Table VII), and for even values of the ionic strength (Table VIII). These interpolated values are graphically represented in Figures III and IV, in which $-\log \gamma$ is given as abscissa and the mole fraction of total acetate as the sodium salt as ordinate. In the one chart the contour lines represent the molecular concentration, in the other the ionic strength of the acetate solution whose P_H is to be calculated.

Summary

1. The dissociation of acetic acid has been studied in the presence of its sodium salt. Inter-ionic forces have been considered by combining the mass law expression for the dissociation of a weak acid with the Debye-Hückel equation for the activity coefficient of an ion. This yields for acetic acid

$$P_{H^+} - \log [(CH_3COO^-)/(CH_3COOH)] = P_K - 0.5\sqrt{\mu}/(1 + \kappa b) + Ks\mu = P_{K'}$$

2. Precise measurements can be made with the hydrogen electrode upon buffer solutions of relatively high molecular concentration but such low ionic strength that specific ion effects are nearly eliminated. Under such circumstances the dissociation constant of the acid can be accurately determined by extrapolation.

3. If 0.3380 is taken as the value of the 0.1 N calomel electrode, these data yield for acetic acid $P_K = 4.73$; Ka = 1.86×10^{-5}. The dissociation constant of acetic acid derived from electromotive force measurements, and this value for the 0.1 N calomel electrode, thus agree with Kendall's estimate from conductivity measurements of 1.85×10^{-5}.

4. The electromotive force measurements that have been made determine the dissociation constant of acetic acid with an error of less than 0.6 millivolts. The value assumed for the 0.1 N calomel electrode thus becomes the controlling factor in determining the dissociation constant of acetic acid by this method.

5. If 0.3357 is taken as the value of the 0.1 N calomel electrode, these data yield $P_K = 4.77$; Ka = 1.7×10^{-5}. Certain of the results are more consistent when calculated by means of this value of the 0.1 N calomel electrode.

6. It is urged that the accumulating data render it desirable both from theoretical and practical considerations to employ a value for the 0.1 N calomel electrode other than 0.3380, and therefore to increase the entire P_H scale. It is suggested that the comparison of electromotive force measurements of the kind here presented, with conductivity measurements upon the same weak acid and its salt, corrected for inter-ionic forces, could form the basis for standardization.

7. The activity coefficients estimated for the acetate anion are inde-

pendent of any assumption regarding the 0.1 N calomel electrode. Values of the salting-out constant, Ks, and of b, have been estimated for solutions varying in molecular concentration from 0.02 to 4 M, and in the mole fraction as CH_3COONa from 0.1 to 0.9.

8. Interpolation tables and graphs are given to facilitate the preparation of buffer solutions of the same ionic strength and varying P_H, or of the same P_H and varying ionic strength.

9. These measurements upon acetate mixtures together with those already published upon phosphate mixtures render it possible to prepare buffer solutions of known ionic strength at any reaction between P_H **3.6** and 7.6.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

THE DECOMPOSITION OF AZO-ISOPROPANE. A HOMOGENEOUS UNIMOLECULAR REACTION

BY HERMAN C. RAMSPERGER[1]

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The decomposition of azomethane was found to be first order at high pressures[2] but at lower pressures a reduction in the rate constant was found.[3] This result has been accounted for on one of the theories (Theory II)[4] of unimolecular gas reactions developed by Rice and Ramsperger.[5] It was to be expected that other azo compounds would also decompose in unimolecular manner and that the higher, more complex azo compounds would maintain the same rate constant to lower pressures than does azomethane. In this research the rate of reaction of azo-isopropane has been determined at initial pressures from 4.60 cm. to 0.025 cm. and at temperatures from 250 to 290°.

Reaction Products

Azomethane reacted principally according to the equation $CH_3NNCH_3 = N_2 + C_2H_6$. A small amount of side reaction could be attributed to either of the following reactions.

$$2CH_3NNCH_3 = 2N_2 + C_2H_4 + 2CH_4$$
$$CH_3NNCH_3 = N_2 + C_2H_4 + H_2$$

The final pressure was 2.04 times the initial pressure instead of exactly 2 times, due to one or both of these side reactions. The complete decomposition of azo-isopropane at constant temperature and constant

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[1] National Research Fellow in Chemistry.

[2] Ramsperger, THIS JOURNAL, **49,** 912 (1927).

[3] Ramsperger, *ibid.,* **49,** 1495 (1927).

[4] Rice and Ramsperger, *ibid.,* **49, 1617** (1927).

[5] Rice and Ramsperger, *ibid.,* 50, 617 (1928).

volume gave an average final pressure of 2.15 times the initial pressure. The main reaction and side reactions analogous to azomethane are

$$C_3H_7NNC_3H_7 = N_2 + C_6H_{14} \quad (1)$$
$$C_3H_7NNC_3H_7 = N_2 + C_3H_6 + C_3H_8 \quad (2)$$
$$C_3H_7NNC_3H_7 = N_2 + C_6H_{12} + H_2 \quad (3)$$

One can distinguish between Side Reactions (2) and (3) by freezing out all of the hydrocarbons with liquid air. From the final pressure value given above and assuming Equation (2), 53.5% of the gas should be condensable, and assuming equation (3) 46.5% should be condensable. Two results of 53.0 and 53.8% show that the final pressure can be accounted for if 85% reacts according to Equation (1) and 15% according to Equation (2).

The Preparation of Azo-isopropane

Azo-isopropane was prepared by the method of Lochte, Noyes and Bailey.[6] Symmetrical di-isopropylhydrazine hydrochloride was prepared by the method of Lochte, Bailey and Noyes.[7] It was recrystallized twice from absolute alcohol. An alkaline solution of the compound was treated with an excess of copper acetate and the azo-isopropane distilled. It was dried with calcium chloride, redistilled and finally was very slowly distilled at 0° through soda lime and calcium chloride in a vacuum line. It was freed from air in the same manner as was azomethane.[2] The supply of gas for some of the decomposition experiments was contained in a 700-cc. bulb which was painted black to prevent possible decomposition by light. For some of the lower pressure experiments a 250-cc. bulb was used with a capillary tube between the bulb and the reaction cell. For the lowest pressure experiments the desired amount of gas was allowed to flow through the capillary into the tubing leading to the cell but was prevented from flowing into the cell by a mercury U-trap. By lowering the mercury in this trap, the gas could be let into the cell and a pressure measurement usually made within ten seconds. The decomposition during this period would be negligible at the lower temperatures but a small correction of at most several per cent. was made at high temperatures, the amount of the correction being usually determined by the final pressure obtained. One sample of azo-isopropane was used for Expts. 1 to 18, inclusive. The bulb was filled from the same liquid four times. The first filling was for Expt. 1, the second for Expts. 2 and 3, the third for Expts. 4 to 8, inclusive, and the fourth from 9 to 18, inclusive. Examination of the results shows that the constants did not vary with the fraction of the sample used. However, a new sample of liquid made from a different sample of di-isopropylhydrazine hydrochloride gave somewhat lower and irreproducible constants at the same pressure range as Expts. 13 to 18. Another

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[6] Lochte, Noyes and Bailey, THIS JOURNAL, 44, 2556 (1922).

[7] Lochte, Bailey and Noyes, *ibid.*, 43, 2597 (1921).

sample was made more carefully and gave the results of Expts. 19 to 2G. These experiments were made to test the effect of increased surface and were sufficiently reproducible for this purpose, but are all somewhat lower and were not used to determine the heat of activation.

Pressure Measurements

The reaction cell and thermostat were the same that were used in the experiments with azomethane.[2] The Pyrex reaction cell is ring-sealed into an outer chamber in which mercury is boiled under a known pressure. The rate of the reaction was determined by pressure measurements with a McLeod gage in much the same way as with azomethane.[3] In this case, however, the McLeod gage and mercury trap were surrounded by an air-bath at a temperature of 80° for Expts. 1 to 18 and 50" for Expts. 19 to 26. This was necessary to prevent condensation of the gas in the capillary of the McLeod gage. The calculation of the partial pressure of azo-isopropane in the reaction cell at the beginning and end of each time interval was the same as in the previous paper.[3] This calculation was made as follows.

Let P be the pressure read on the gage. Let the pressures in the reaction cell be designated as follows: P', the pressure before the reading was made; P^W, the pressure after the reading was made; P'_A, the partial pressure of azo-isopropane before each reading; P''_A, the partial pressure of azo-isopropane after each reading. Let V be the volume of the reaction chamber, V_1 the volume of the trap and V_2 the total volume of the McLeod gage. Let T_1 be the temperature of the trap and gage and T_2 the temperature of the reaction cell. Let N_1 be the number of moles of gas in the trap and N_2 the number of moles in the reaction cell. We can calculate P'' in terms of P and the temperature and volume constants as follows. $PV_1 = N_1RT_1$, $PV = N_2RT_2$, $P^WV = (N_1 + N_2)RT_2$. Blirninating N_1 and N_2 we find $P'' = P(V_1T_2/VT_1 + 1)$. P' may be calculated as follows. Let N_3 be the number of moles passing into the gage only, when the mercury is lowered for a reading. Let A P be the increase in pressure read on the gage in two successive readings. Then $\Delta PV_2 = N_3RT_1$ and $P_1'V = (N_1 + N_2 + N_3)RT_2$; $P' = P^W + \Delta PV_2T_2/VT_1$. Now the increase in pressure in the reaction cell, after one reading was made at time t and before the next reading at time t', is $P'_{t'} - P''_t$. If this increase be divided by 1.15, we get the change in azo-isopropane pressure. Therefore we have the relation $P'_{At'} = P''_{At} - (P'_{t'} - P''_t)/1.15$; also, $P''_{At} = P'_{At}\ P''_t/P'_t$. The first order rate constants were then calculated from the relation $K = \log_{10} P''_{At}/P'_{At'}$ X $2.303/(t' - t)$, where t and t' are given in seconds.

Experimental Results

A summary of all of the experiments except Expts. 10 and 15, in which some gross error was made, is given in Table I and the complete data of three typical experiments are given in Table II.

The $\log_{10}$ of the average constant at each temperature is plotted against the reciprocal of the absolute temperature in Fig. 1. The slope of the straight line multiplied by 2.303 R is the "heat of activation," Q, as given by the Arrhenius expression for the temperature coefficient of reaction rate which is $(d \ln K/d)1/T = Q/R$. The intercepts of the straight line

TABLE I

SUMMARY OF ALL EXPERIMENTS

Expt. no.	Temp., °C.	Init. pressure, cm.	Av. K X 10^3	Expt. no.	Temp., °C.	Init pressure, cm.	Av K X 10^3
12	250	1.771	0451	7	280	3.080	3 8 8
13	250	388	.461	8	280	.770	3 96
18	250	0786	467	11	290	.3685	7 96
4	260	4.60	1.03	16	290	.0919	7 46
1	260	4.09	98	24	270	.137	1 90
2	260	2.94	1OG	25	270	.113	1.86
3	260	1.75	.98	19	270	.106	1.84
17	260	.0926	1.02	21	270	.097	1.85
5	270	3.515	1 9 9	23	270	.0850	1.84
9	270	1.917	2.01	22	270	.0550	1.95
6	270	,649	2.14	26	270	.0283	1.80
14	270	,0857	2.04	20	270	.0257	1 8 1

TABLE II

COMPLETE DATA OF THREE EXPERIMENTS

Expt. 5. V_1T_2/VT_1 = 2 8 X 543/2.10 X 353 = 0.020; V_2T_2/VT_1 = 11.14 X 543/2 10 X 353 = 0.082; decomposition in filling cell = 0.035 cm.

t, min.	0	3	6	9	12	17	35
P, cm.	3.480	4630	5.390	5.885	6.220	6.555	7.000
P''	3.550	4.725	5.500	6.005	6.345	6.690	7.140
P'	...	4.819	5.562	6.056	6.372	6.717	7.148
P'_A	...	2.377	1.602	1.099	.772	.446	.021
P''_A	3.480	2.330	1.582	1.091	,769	.444	.021
K(× 10^3)	..	2.12	2.08	2 0 2	1.92	1.82	. .

Expt 25 V_1T_2/VT_1 = 2.8 X 543/168 X 323 = 0.028; V_2T_2/VT_1 = 8.90 × 543,168 X 323 = 0 089

t, min	0	2	4	6	9	16
P, cm.	0 110	0.132	0.152	0.165	0.183	0.208
P″	,113	.136	.156	.170	.188	.214
P'	...	.138	.158	.171	.190	.216
P'_A		.091	.071	.057	.040	.016
P''_A	.113	.090	.070	.057	.040	.016
K (X 10^3)	...	1.80	1.98	1.71	1.97	...

Expt. 17. V_1T_2/VT_1 = 2.8 X 533j210 X 353 = 0.020; V_2T_2/VT_1 = 8.90 X 533/210 X 353 = 0 064

t, min.	0	4	8	12	19
P, cm.	0.0908	0.1102	0.1260	0.1396	0.1580
P"	.0926	.1127	.1285	.1424	.1612
P'	...	.1140	.1296	.1433	.1624
P'_A	...	.0740	.0585	.0452	.0275
P''_A	.0926	.0732	.0581	.0449	.0273
K(× 10^3)	...	.93	.93	1.05	1.17

are for $1/T$ = 0.00177 $\log_{10}$ K = —2.06 and for $1/T$ = 0.00192 $\log_{10}$ K = —3.40. Q is found to be 40,900 cal. per mole. The rate constant $K = 5.6 \times 10^{13} \times e^{-\frac{40900}{RT}}$.

Expts. 24, 25 and 26 were made with enough small Pyrex tubing in the cell to make the surface six times as great. They are to be compared to five other experiments at that temperature and from the same sample, namely, 19, 20, 21, 22 and 23. The average rate constant of these five is 1.86×10^{-3} and of the three with tubing 1.85×10^{-3}. It is apparent that the reaction rate is not influenced by increase of wall surface and that the reaction is therefore homogeneous. It is also evident from the two experiments at the lowest, pressures, that is, Expts. 20 and 26, that within experimental error there is no change in the rate constant at this low pressure.

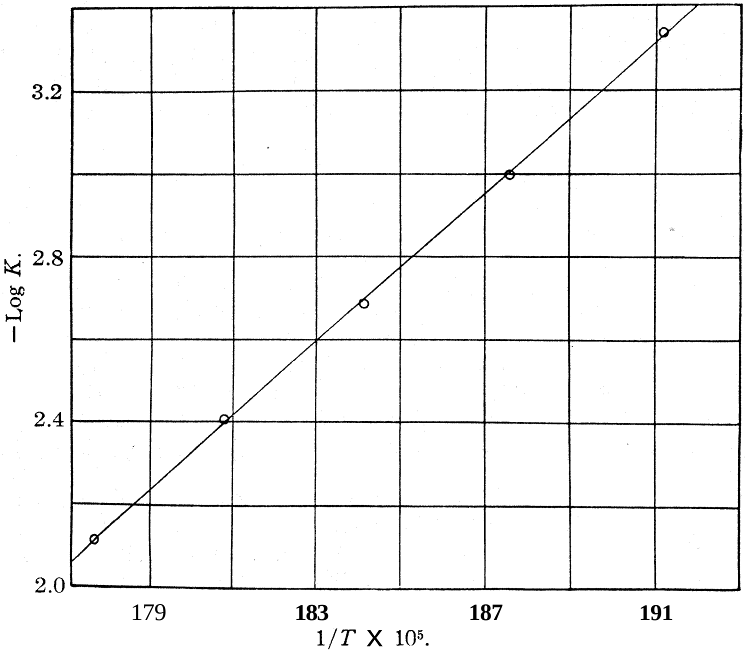

Fig. 1.

Theoretical

The results indicate that the more complex azo-isopropane maintains a constant value of the rate constant to low pressures where azomethane deviates greatly from the high pressure rate. In the case of azomethane the rate constant was appreciably below the high pressure rate constant at 4 cm. initial pressure and became steadily lower as the initial pressure was decreased until at 0.025 cm. the rate had dropped to 22% of the high pressure value when the temperature was 290° and to 10% for 330°.[3] It has been found that Theory II of Rice and Ramsperger[4] explains all of the rate constants of azomethane over the 3000-fold pressure range if 25 internal degrees of freedom are used.[5] Theory I by the same authors does not fit the data Twenty-five degrees of freedom is a reasonable value for this molecule. The specific heat (C_v) of the gas would then be expected to be about 28 cal. per mole at a temperature of 300°, since each degree of freedom is equivalent to $^1/_2R$ cal. per mole and the three translational degrees of freedom are to be added. The specific heat of azomethane is not known but acetone might be expected to have a similar specific heat. Its specific heat (C_v) at 26 to 110° is 18.1 cal. and at 129 to 233° it is 21.9 cal. per mole, so that the twenty-five degrees of freedom required to fit the data is a reasonable value. If we apply either Theory I or Theory II to azo-isopropane, we find that 45 to 50 degrees of freedom will be required if the same rate constant is to be maintained to 0.0257 cm. initial pressure. The very large specific heat which is required is not impossible for such a large molecule. hzomethane has 10 atoms and 10 chemical bonds while azo-isopropane has 22 atoms and 22 chemical bonds, so that we might expect a specific heat about twice as great for azo-isopropane. Theory I is an extension of the theory of Hinshelwood and Lindemann[8] so that their theory likewise requires this large number of degrees of freedom. The theory of Fowler and Rideal was used by Bernard Lewis[10] to explain the decomposition of azomethane before the data on azomethane at low pressures were published. This theory has not been developed so far as to show the manner in which the rate will change at low pressures. It requires fewer degrees of freedom but has the disadvantages pointed out by Tolman, Yost and Dickinson.[11]

Other possible explanations of the rate of unimolecular reactions are the chain mechanism and the radiation hypothesis. A reaction chain mechanism has been shown to be impossible in the case of most unimolecular reactions[12] and it was shown by the author[13] that in the photochemical decomposition of azomethane with a light photon of much higher energy than the heat of activation, only two molecules were decomposed per photon absorbed. The radiation theory of chemical reaction has been definitely disproved in at least one instance by Lewis and Mayer.[14]

The theories which are still capable of explaining all of the first order gas phase reactions are all collision theories which in most instances depend upon rather large internal energies. It is noteworthy that these theories differ in the assumptions concerning energy transfer between molecules at collision and energy transfer within the molecule. Three cases may be mentioned.

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[8] Hinshelwood and Lindemann, *Proc. Roy. Soc. (London)*, **113A,** 230 (1926).

[9] Fowler and Rideal, *ibid.*, **113A,** 570 (1927).

[10] Lewis, *Proc. Nat. Acad. Sci.*, 13, 546 (1927).

[11] Tolman, Yost and Dickinson, *ibid.*, 13, 188 (1927); Lewis, *Science*, 66,331 (1927), has corrected an error in this paper.

[12] Lewis and Smith, THIS JOURNAL, 47, 1508 (1925); Tolman, *ibid.*, 47, 1524 (1925).

[13] Ramsperger, *ibid.*, 50, 123 (1928).

[14] Lewis and Mayer, *Proc. Nat. Acad. Sci.*, 13,623 (1927).

First, the theories of Hinshelwood and Lindemann,[8] and Theory I of Rice and Ramsperger, in which the *total energy* of the molecule should equal or exceed a minimum energy in order that the molecule be activated. Some of them react, but the chance of reaction is independent of the amount of energy in excess of this minimum. It is assumed that the rate of activation is equal to what the rate of deactivation would be under equilibrium conditions. The rate of deactivation is calculated on the assumption that *every collision of an activated molecule results in deactivation and the ordinary kinetic theory radius is used in this calculation.*

Second, the theory of Fowler and Rideal,[9] which requires that *if the sum of the energies of two colliding molecules is equal to or exceeds a certain minimum of energy, all of this energy is transferred to one molecule which is then activated.* Lewis[11] shows that in the case of N_2O_5 this leads to *a deactivation radius of* 6.07×10^{-6} *cm.*

Third, Theory II of Rice and Ramsperger,[4] in which the rate of deactivation and of activation is calculated as in Theory I. *In addition it requires that a particular degree of freedom get a minimum of energy after which reaction occurs immediately. It must be possible for energy to be redistributed among the various degrees of freedom within the molecule between collisions.*[15]

It seems likely that the conditions of energy transfer differ widely in different molecules and that as a consequence there may be reactions which will fit each theory and some reactions that are intermediate in type and cannot be fitted exactly by any of the above theories. Two evidences of variation in energy transfer may be cited.

First, the experiments of Stuart,[16] which show that the quenching of the resonance fluorescence of mercury differs very widely for different gases, being greatest for H_2 and least for He. Second, the experiments of Hinshelwood show that of a number of inert gases only hydrogen can maintain the high pressure rate constant of a "quasi" unimolecular reaction at low pressures. It may be expected that the fewer quantum states of simpler molecules will introduce special restrictions of energy transfer which would be far less likely to occur in the complex molecules which decompose in unimolecular manner.

Summary

The thermal decomposition of azo-isopropane has been studied at temperatures from 250 to 290°, at initial pressures from 4.60 cm. to

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[15] A fourth type which is not quite comparable with the three cases listed above is the theory of J. J. Thomsen [*Phil.* Mag. [7] 3, *241* (1927)], in which energy may be transferred from the fields of neighboring molecules. The energy of a given molecule "waxes and wanes" and thus at some instant may get sufficient excess energy from the field to cause reaction.

[16] Stuart, *Z. Physik,* 32, *262 (1925).*

0.025 cm. and with increased wall surface. The reaction was found to be homogeneous and unimolecular at all pressures.

The heat of activation as given by the Arrhenius expression for the temperature coefficient of reaction rate is 40,900 cal. per mole. The rate constant is given by the expression $K = 5.6 \times 10^{13} \times e^{\frac{-40{,}900}{RT}}$.

A discussion of these results in relation to various theories of reaction rate is given. Theory II of Rice and Ramsperger would require that the rate constant of the reaction become smaller at pressures below 0.025 cm. if the azo-isopropane molecule had 45 to 50 degrees of freedom, It is thought likely that the specific heat of azo-isopropane would be large enough to permit this number of degrees of freedom.

STANFORD UNIVERSITY, CALIFORNIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY. CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 162]

THE REDUCTION POTENTIAL OF SELENIUM AND THE FREE ENERGY OF AQUEOUS SELENOUS ACID

BY HERMAN F. SCHOTT, ERNEST H. SWIFT AND DON M. YOST

RECEIVED DECEMBER 5, 1927 PUBLISHED MARCH 7, 1928

Introduction

The fact that selenous acid, H_2SeO_3, is reduced to elementary selenium by iodides in acid solutions is well known and is made use of in analytical methods for the determination of selenium.[1] The reduction, however, is quantitative only in moderately strong acid solutions. It was found, as a result of a number of preliminary experiments, that in more dilute acid solutions the substances taking part in the reaction are present in measurable amounts when equilibrium is attained.

In this paper are described equilibrium measurements at 25° for the following reaction, together with the thermodynamic quantities calculated from them, $Se(s) + 2I_2(s) + 3H_2O(l) = H_2SeO_3(aq) + 4H^+ + 4I^-$.

We wish to express here our appreciation of the many useful suggestions made by Professor A. A. Noyes. The investigation was aided on the financial side by funds granted to him by the Carnegie Institution of Washington.

Outline of the Investigation

The reaction mixtures were prepared by mixing standard solutions of selenous acid, potassium iodide, perchloric acid and water in 250cc. volumetric flasks and transferring the contents to glass-stoppered bottles

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[1] Muthman and Schäfer, *Ber.*. 26, 1008 (1893); Gooch and Reynolds, *Z. anorg. Chem.*, 10,248 (1895).

containing solid iodine and black selenium[2] Some precautions were taken to exclude atmospheric oxygen, but it was never entirely eliminated, as will appear below. The bottles were rotated in a thermostat at 25° for at least one week, the preliminary experiments having shown that equilibrium is attained within this time.

Preparation of the Materials

Selenium.—Pure, sublimed selenium dioxide was dissolved in a slight excess of dilute sodium hydroxide solution, and the resulting mixture was treated with sodium thiosulfate and heated to boiling for several hours. The precipitate of elementary selenium which formed was filtered off, washed with water and alcohol, and finally dried in a current of air. This procedure yields the black selenium, which is stable at ordinary temperatures[3]

Selenous Acid.—Commercial black powdered selenium was dissolved in nitric acid, evaporated to dryness and heated until the yellow color disappeared. The residue was then dissolved in water, the solution filtered, evaporated to dryness and the residue sublimed.[4] The stock solution of selenous acid was prepared by dissolving the fine, needle-like crystals in water.

Hypochlorous Acid.—This was prepared by passing chlorine through a mixture of water and solid mercuric oxide for about one hour and distilling in a current of air the resulting solution, after removing the excess of mercuric oxide.[5] The distillate containing the hypochlorous acid was absorbed in ice-cold water.

Other Materials.—The iodine, potassium iodide and perchloric acid used were the purest trade preparations.

Analysis of the Equilibrium Mixtures

Samples of the liquid phase, free from any solid, were removed from the bottles by forcing the solutions into a 50cc. pipet equipped with an asbestos filter, compressed air being used which had been passed over solid iodine.

Two samples were required for a complete analysis of each equilibrium mixture. One of them was used for the determination of the iodine and selenous acid, the other for the determination of the acid. The standard solutions were all about 0.1 N. The two methods of analysis used were as follows.

Determination of Iodine and Selenous Acid.—A 50cc. sample, immediately after its removal from the reaction mixture, was run into a glass-stoppered flask containing 10–30 cc. of standard hydrazine sulfate solution and 13–16 millimoles of Na_2HPO_4. The excess of iodine remaining

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[2] Beckmann and Grünthal, Z. *anorg. chem.*, *84*, **97** (1913), have shown that selenium and iodine form no compounds, mixed crystals or solid solutions.

[3] See Abegg-Auerbach-Kappel, "Handbuch der anorganischen Chemie," Band IV, 1 Abt., 1 Hälfte, S. Hirzel, Leipzig, 1927. The product used here was a fine black powder.

[4] Sacc, *Ann. chim. phys.*, [3] *21*, **119** (1847); Janneck and Meyer, Z. *anorg. allgem. Chem.*, *83*, **51** (1913).

[5] Bray and Cuy, THIS JOURNAL, 46,858 (1924).

was then titrated with more of the standard hydrazine solution.[6] In this mixture, which is practically neutral, the iodine is reduced quantitatively to iodide by the hydrazine, while selenous acid is not appreciably affected by either the iodide or hydrazine during the time required for the analysis.

To the sample after the hydrazine titration, there was added 4–4.5 cc. of 6 N sulfuric acid and an excess (35–60 cc.) of the standard hydrazine, and the resulting mixture was kept at about 100° for three to four hours.[7] After cooling and filtering the solution it was made neutral with 4-6 cc. of 4 N sodium hydroxide, and excess (10–25 cc.) of standard hypochlorous acid added and after five minutes the liberated iodine was titrated with the standard hydrazine. In this process selenous acid is reduced to elementary selenium by the hydrazine and iodide in the hot acid solution. The hypochlorous acid added to the neutral solution quantitatively oxidizes the excess of hydrazine and also liberates iodine, the latter then being determined with the standard hydrazine.

Determination of the Strong Acid.—To determine in the equilibrium mixtures the "strong acid" present (that is, the acid in other forms than selenous acid) a 50cc. sample of the equilibrium mixture was introduced into a flask containing 10–25 cc. of standard thiosulfate and an excess (25–55 cc.) of standard hydrocarbonate solution. The rest of the iodine present was then just decolorized by titrating it with more of the standard thiosulfate. The resulting solution was titrated with standard hydrochloric acid, using a mixture of methyl red and methylene blue as indicator. A blank containing only selenous acid in the same amount that was present in the sample was treated with an excess of standard hydrocarbonate and the excess determined with standard hydrochloric acid.

It was necessary to decolorize the iodine in order to see the color changes of the indicator. The reaction between iodine and thiosulfate in hydrocarbonate solution produces not only tetrathionate, but also some sulfuric acid according to the reaction[8]

$$2S_2O_3^{=} + I_2 = S_4O_6^{=} + 2I^-, \text{ and}$$
$$S_2O_3^{=} + 4I_2 + 5H_2O = 2SO_4^{=} + 10H^+ + 8I^-$$

It was possible to make a correction for the acid formed by the second reaction, since the total amount of iodine present was known from the results of the hydrazine titration, namely, since for each equivalent of iodine that reacts in the second way there would be a decrease of $^7/_8$ mole in the thiosulfate consumed, and since this reaction produces $^{10}/_8$ equivalent of hydrogen ion for each equivalent of iodine, the acid produced is $^{10}/_7$ times the difference between the equivalents of iodine present and the mole of thiosulfate used. Making this correction and also that resulting from

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[6] Stolle, J. *prakt. Chem.*, [2] 66, 332 (1902); *Chem. Zent.*, 1903, II, 1340.

[7] Strecker and Schartow, *Z. anal. Chem.*, 64, 218 (1924).

[8] Abel, *Z. anorg. Chem.*, 74, 395 (1912); Topf, *Z. anal. Chem.*, 26, 184 (1887).

the blank analyses of the selenous acid alone, the concentration of the strong acid in the equilibrium mixture was calculated. Duplicate analyses always agreed within 1%.

Density Measurements.—In order that the volume concentrations might be converted into weight concentrations, a definite volume of each equilibrium mixture (free from solid) was weighed.

Calculation of the Equilibrium Concentrations

The concentration of strong acid and the total concentration of selenous acid were calculated directly from the analytical data. To obtain the concentration of hydrogen ion due to both the free acid and the dissociated selenous acid it was necessary to employ the first ionization constant of 56-60 selenous acid. This has been determined by Blanc[9] to be 2.7×10^{-3}. The second ionization constant (5×10^{-8}, according to Blanc) is small enough to be neglected at this point. The concentration of undissociated selenous acid was obtained as follows. If a is the concentration of strong acid, b the total concentration of selenous acid and x that of the dissociated selenous acid, then $a + x$ is the concentration of H^+ in the solution, x that of $HSeO_3^-$, and $b - x$ that of the undissociated selenous acid, H_2SeO_3. Substituting these quantities in the expression $(H^+)(HSeO_3^-) = 2.7 \times 10^{-3} (H_2SeO_3)$, the value of (H_2SeO_3) is obtained.

The concentration of iodide ion was obtained by first subtracting from the total iodine concentration as determined by analysis the solubility of iodine in water and then multiplying the difference, which is the concentration of tri-iodide ion, I_3^-, by the known value of the iodide-tri-iodide ratio for a solution saturated with respect to iodine and having the same total iodide (iodide plus tri-iodide) concentration as the equilibrium mixture. The value of the ratio for each mixture was interpolated from the results given by Bray and MacKay,[10] which are in part as follows.

Total iodide $(I^-) + (I_3^-)$	0.1000	0.020	0.010
Ratio $(I^-):(I_3^-)$	0.99	1.04	1.06

Their value for the solubility of iodine in water (1.33 millimolal) was also used.

The activity of the undissociated selenous acid was taken equal to its concentration. The activity coefficient of the hydriodic acid was found by interpolating the activity coefficient corresponding to the ionic strength of each equilibrium mixture from the table given by Pearce and Fortsch,[11] some of whose results are as follows.

Molality of HI	0.050	0.100	0.200
Activity coefficient, γ	0.868	0.846	0.834

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[9] Blanc, *J. chim. phys.*, 18, 28 (1920).

[10] Bray and MacKay, THIS JOURNAL, 32, 914 (1910).

[11] Pearce and Fortsch, *ibid.*, 45, 2852 (1923).

The ionic strengths of the equilibrium mixtures were taken as the total molality of the cations since all ions present at appreciable concentrations were univalent.

Composition of the Equilibrium Mixtures

The initial compositions of the mixtures, expressed in millimoles per liter, are given in Table I. Solid iodine and solid black selenium were always present initially and when equilibirum was attained.

TABLE I

INITIAL CONCENTRATIONS OF THE MIXTURES

Expt.	1	2	3	4	5
KI	4.15	87.88	0.00	0.00	58.88
$HClO_4$	50.15	39.67	.00	9.87	26.50
H_2SeO_3	0.00	10.00	.00	14.00	25.00

In Table II are given the concentrations of the various constituents present when equilibrium was attained. The auxiliary data necessary to calculate the equilibrium constant are also included. All concentrations are expressed in millimoles per liter. The values for the equilibrium constant, K, were calculated by the expression

$$K = (H_2SeO_3)(H^+)^4(I^-)^4\gamma^8/w^9$$

In this expression (H_2SeO_3) is the concentration of undissociated selenous acid, γ the activity coefficient of hydriodic acid and w the weight of water per liter of solution. This last factor served to change the values of the equilibrium concentrations given in the table from millimoles per liter of solution to moles per kilogram of water.[12]

TABLE II

FINAL CONCENTRATIONS OF THE EQUILIBRIUM MIXTURES AT 25°

Expt.	1	2	3	4	5
(ΣI_3)(deter.)	21.42	43.93	27.23	22.57	34.86
(Is–) (calcd.)	20.15	42.60	25.99	21.24	33.53
Ratio, $(I^-)/(I_3^-)$	1.022	0.996	1.014	1.020	1.006
(I–) (calcd.)	20.59	42.43	26.35	21.67	33.73
Strong acid (deter.)	74.34	34.02	51.62	50.78	31.94
(H^+) (calcd.)	74.66	34.86	52.26	52.09	34.19
(ΣH_2SeO_3) (deter.)	9.33	11.65	13.03	26.62	30.82
(H_2SeO_3) (calcd.)	9.00	10.81	12.37	25.31	28.57
G. solution per liter	1008.26	1019.66	1008.78	1008.90	1016.10
G. solute per liter solution	17.03	30.87	15.29	15.61	26.30
G. water per liter of solution	991.2	988.8	993.5	993.3	989.8
Concentration of cations	78.81	122.7	52.26	52.09	93.07
Activity coeff. of HI	0.853	0.841	0.866	0.865	0.848
K X 10^{14}	1.525	1.433	1.492	1.369	1.482
					Mean 1.46

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[12] Owing to the fact that oxygen was always present initially and this caused the liberation of some iodine in the acid-iodide mixtures, the final acid concentrations cannot be estimated from the changes in the concentrations of selenous acid. In all cases the true equilibrium concentrations were taken to be those determined by analysis.

The Equilibrium Constant

The agreement among the values for the equilibrium constant is very satisfactory, especially when it is considered that the large exponents occurring in the mass action expression cause small errors (always less than 1%) in the analytical results to be greatly magnified in the values for the equilibrium constant.

As the best value of the equilibrium constant $K = (H_2SeO_3)(H^+)^4(I^-)^4$ the mean value 1.46×10^{-14} may be adopted. In this value the concentrations are expressed in moles per 1000 g. of water, and activities of H^+ and I^- are used in place of their concentrations.

Free Energies and Reduction Potential

From the equilibrium constant of the reaction the free energy decrease accompanying it was calculated by the well-known expression $-\Delta F^\circ = RT$ In K. The result is expressed by the equation

$$Se(s) + 2I_2(s) + 3H_2O(l) = H_2SeO_3 + 4H^+ + 4I^- - 18{,}880 \text{ cal.} \qquad (1)$$

Now, according to Lewis and Randall,[13] at 25°

$$2I_2(s) + 2H_2(g) = 4H^+ + 41 + 49{,}440 \text{ cal.} \qquad (2)$$

Subtracting we get

$$Se(s) + 3H_2O(l) = H_2SeO_3 + 2H_2(g) - 68{,}320 \text{ cal.} \qquad (3)$$

This is, however, the reaction that occurs in the cell $Se(s), H_2SeO_3 || H^+, H_2(g)$. Its free energy decrease therefore corresponds to the reduction potential of $Se(s) + 3H_2O(l) = H_2SeO_3 + 4H^+ + 4E-$. Multiplying the free energy value by 4.185 (to change it to joules) and dividing by 4 X 96,500 coulombs, we get for this reduction potential the value –0.740 volt.

We may find also the free energy of 1 M H_2SeO_3 (un-ionized) by adding to Equation (3) the following[13]

$$3H_2(g) + 3/2\ O_2(g) = 3H_2O(l) + 169{,}680 \text{ cal.}$$

Hence

$$Se(s) + 3/2\ O_2(g) + H_2(g) = H_2SeO_3 + 101{,}360 \text{ cal.} \qquad (4)$$

That is, ΔF°_{298} for H_2SeO_3 (un-ionized) is –101,360 cal.

From the first and second ionization constants of selenous acid, which are 2.7×10^{-3} and 5×10^{-8} according to Blanc,[9] we get

$$H_2SeO_3 = H^+ + HSeO_3^- - 3{,}510 \text{ cal.}$$
$$H_2SeO_3 = 2H^+ + SeO_3^= - 13{,}470 \text{ cal.}$$

Adding separately each of these equations to Equation (4) gives

$$Se(s) + 3/2\ O_2(g) + H_2(g) = H^+ + HSeO_3^- + 97{,}850 \text{ cal.}$$
$$Se(s) + 3/2\ O_2(g) + H_2(g) = 2H^+ + SeO_3^= + 87{,}890 \text{ cal.}$$

That is, ΔF°_{298} is –97,850 cal. for $HSeO_3^-$, and –87,890 cal. for $SeO_3^=$

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[13] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 607.

Summary

In this paper are described determinations of the equilibrium of the reaction $Se(black) + 2I_2(s) + 3H_2O = H_2SeO_3 + 4H^+ + 4I^-$ at 25". The equilibrium constant $K = (H_2SeO_3)(H^+)^4(I^-)^4$ was found to be 1.46×10^{-14}, expressing the concentrations in moles per 1000 *g.* of water and using the activities of H^+ and I^- in place of their concentrations.

From this constant and existing thermodynamic data the reduction potential of $Se(black) + 3H_2O(l) = H_2SeO_3 + 4H^+ + 4E^-$ was calculated to be −0.740 volt, showing that the reducing power of selenium (at 1 *M* H^+ concentration) is about the same as that of Fe^{++}, Fe^{+++} (−0.747), and intermediate between those of I^-, $I_2(s)$ (−0.536) and Ag, Ag^+ (−0.800).

The corresponding free energies (AF^{o}) at 25° of H_2SeO_3, $HSeO_3^-$, and $SeO_3^=$ at 1 *M* were found to be −101,360, −97,850 and −87,890 calories, respectively.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NON-RESIDENT LECTURESHIP IN CHEMISTRY, BAKER LABORATORY, CORNELL UNIVERSITY]

TRANSITION CELLS OF THE SIXTH CLASS

BY ERNST COHEN AND ERNEST J. JOSS

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A transition cell may be defined broadly as any reversible galvanic element containing a solid substance which may exist in a number of modifications.

While five different classes of such elements have been treated theoretically as well as experimentally by Ernst Cohen and his co-workers,[1] transition cells of the sixth class have not, as yet, been experimentally realized. Such an element is to contain a depolarizer which possesses a transition point. This paper deals with a transition cell of this type, the depolarizer being silver iodide.

Experimental

It was thought best to use a cell with a standard electrode, rather than two electrodes of silver iodide, one stable and the other metastable. With the former type of cell the temperature-e.m.f. curve may be run over a wide range of temperatures, the transition temperature being indicated by a sudden change in the temperature coefficient of e.m.f. The choice of an electrolyte afforded some difficulty. The use of aqueous solutions was impractical, since the temperatures to be used were as high as 175". The solvent finally chosen was fused calcium chloride hexahydrate. The boiling point of this substance was within the temperature range over

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[1] Ernst Cohen, "Physico-chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., New York, 1926, p. 151 ff.

which the experiments were to be run, so a closed apparatus was necessary. The melting point was 29.9" which was well below all experimental temperatures.

The cells were made up according to the following scheme:

$$\mathrm{Ag_{(s)} - AgI_{(s)}} \left| \begin{array}{c} \mathrm{CaCl_2.6H_2O_{(l)}} \\ \mathrm{AgI_{(c_1)}} \\ \mathrm{PbI_{2(c_2)}} \end{array} \right| \mathrm{Pb_{(s)}}$$

The design of the cell is shown in Fig. 1.

A, the positive pole, is a silver iodide electrode made after the method of Jones and Hartmann.[2] B is the standard electrode, made of pure lead. The two electrodes were joined to the H-cell by means of inner seals. A side tube was provided for introducing the electrolyte. The whole cell, made of heavy Pyrex glass, was quite small and compact.

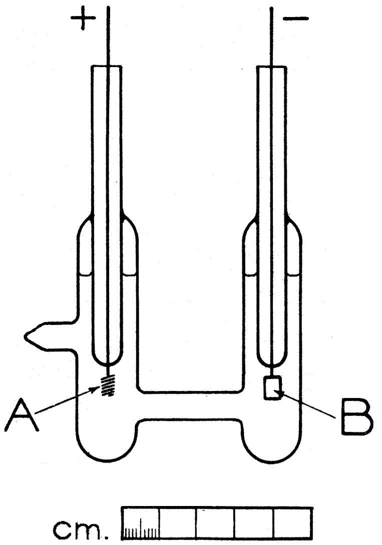

Fig. 1.

The electrolyte was molten calcium chloride hexahydrate saturated with both silver iodide and lead iodide at 40°. This solution was introduced into the cell through the side tube, which was subsequently sealed off at a constriction provided for this purpose. It is probable that little if any silver iodide was in solution around the lead electrode, due to interaction with the metallic lead.

The cell was completely immersed in a bath of Crisco, a hydrogenated cooking fat. This bath was placed in an air thermostat for temperature control. The air thermostat was built from an ordinary 50 X 45 X 30 cm. gas oven. This was covered on all sides with a 2 cm. layer of sheet asbestos. Air circulation was maintained within the oven by means of a 20cm. four bladed fan. The shaft driving this fan ran in a bearing fastened in a board across the top of the oven. The fan was driven at about 1400 r.p.m. by a small electric motor. A separate motor ran a stirrer for the oil-bath. The stirrer passed through the top of the oven and was connected directly to the motor. The speed of this motor was approximately 200 revolutions per minute.

The temperature of the oven was controlled by means of a spiralled, mercury in glass, thermal regulator. The capillary tube at the top of the regulator was passed through the top of the oven and protruded eight centimeters up into the outside air. This precluded the dangers of mercury at high temperatures. The temperature was measured by means of a thermometer immersed in the oil-bath, so that the mercury bulb was very close to the transition element. The thermometers used were very long so that the scale was visible above the oven. These thermometers were graduated with 0.1° divisions and calibrated against standard thermometers calibrated by the Physikalisch-Technische Reichsanstalt at Charlottenburg-Berlin.

The oven was fitted with a main electrical heating unit, consisting of a number of coils of nichrome wire wound on Pyrex glass tubes, and an auxiliary heating unit made by winding a single coil of nichrome wire on asbestos board. One end of the main

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[2] Jones and Hartmann, THIS JOURNAL, 37, 755 (1915).

heating coil was attached to one end of the auxiliary coil, from which junction a common lead was run to the source of current (110 A.C.). The other end of the main heating coil was connected, in series with a variable rheostat (Ward-Leonard, Type RLR 156) and an ammeter (Weston, 10-ampere range, with 1.5 multiplier), to the source of current. The other end of the auxiliary coil was connected, in series with a fixed resistance and a relay, to the source of current. Both circuits were equipped with knife switches so that they might be operated independently. The relay in the auxiliary circuit was governed by the mercury thermo-regulator and a four-volt source of current. The resistances were fixed so as to cause the main heating coil alone to raise the temperature to about five degrees below the desired temperature; while the auxiliary coil, if the circuit were kept closed, would further raise the temperature to about five degrees above that desired.

The leads from the transition cell were carried out through small glass tubes passing through the side of the oven.

The vibration of the stirrers increased the sensitivity of the thermo-regulator markedly.

With the thermostat described above, temperatures constant to within 0.1° for long periods of time were obtainable.

The electromotive force of the cell was measured by means of the Poggendorff compensation method. A Leeds and Northrup student potentiometer was used in connection with a quite sensitive galvanometer. The standard of electromotive force was a Weston cell.

The method used was to start measurements at the lower end of the temperature range and so regulate the current through the main heating element as to have the temperature rise approximately one degree centigrade every five minutes. The electromotive force was measured for every half degree rise in temperature, the potentiometer being balanced against the standard cell every few readings. When the temperature had risen as high as was desired, the current was so adjusted as to allow cooling at the same rate as the heating. Measurements were again made in the same manner as with rising temperature.

The cell came to equilibrium very rapidly under the conditions of the experiment. This was proved by the fact that the electromotive forces measured with rising temperature checked those with falling temperature within experimental error.

Each of the two runs shown in the following tables was completed without interruption. A different cell was used in each run.

Table I gives the data for the first cell, which we shall designate as Cell I. In this table t refers to the actual temperature in centigrade degrees and E to the electromotive force of the cell in volts. The points indicated by asterisks are those arbitrarily chosen for calculations.

TABLE I

DATA FOR CELL I

t	*E*	*t*	*E*	*t*	*E*	*t*	*E*
128.07	0.2599	129.41	0.2603	141.40	0.2670	152.00	0.2724
120.33	.2556	129.82	.2605	*141.97	.2673	*152.70	.2726
117.91	.2543	130.30	.2607	142.82	.2678	154.00	.2731
120.90	.2558	*130.70	.2610	143.31	.2682	154.75	.2735
118.70	.2547	131.31	.2613	*144.30	.2687	155.40	.2738
119.47	.2555	131.95	.2616	145.10	.2691	*155.95	.2740

TABLE I (*Concluded*)

t	*E*	*t*	*E*	*t*	*E*	*t*	*E*
119.62	,2557	132.78	.2621	145.78	.2695	156.55	.2743
121.50	.2560	133.38	.2625	146.19	.2698	157.10	.2745
122.07	.2563	134.42	.2630	146.90	.2701	157.65	.2747
122.93	.2567	135.25	.2634	*134.28	.2631	*158.20	.2750
123.50	.2570	135.80	.2637	144.70	.2687	159.00	.2753
*124.13	.2573	136.25	.2640	145.75	.2694	*159.25	.2756
124.71	.2576	136.80	.2643	146.38	.2698	161.20	.2762
125.35	.2579	*137.30	.2646	146.90	.2701	*161.80	.2765
125.78	.2582	137.97	.2650	*147.30	.2705	167.80	.2794
126.29	.2585	138.32	.2653	*149.00	.2710	167.70	.2794
126.72	.2588	139.00	.2656	149.50	.2712	168.18	.2795
127.20	.2590	139.62	.2660	150.60	.2716	169.20	.2803
127.80	.2594	140.12	.2663	150.80	.2718	169.60	.2810
*128.28	.2596	140.70	.2666	151.17	.2720		

These data when plotted give the graph shown in Fig. 2. The ordinates are electromotive forces in volts and the abscissas are temperatures in centigrade degrees.

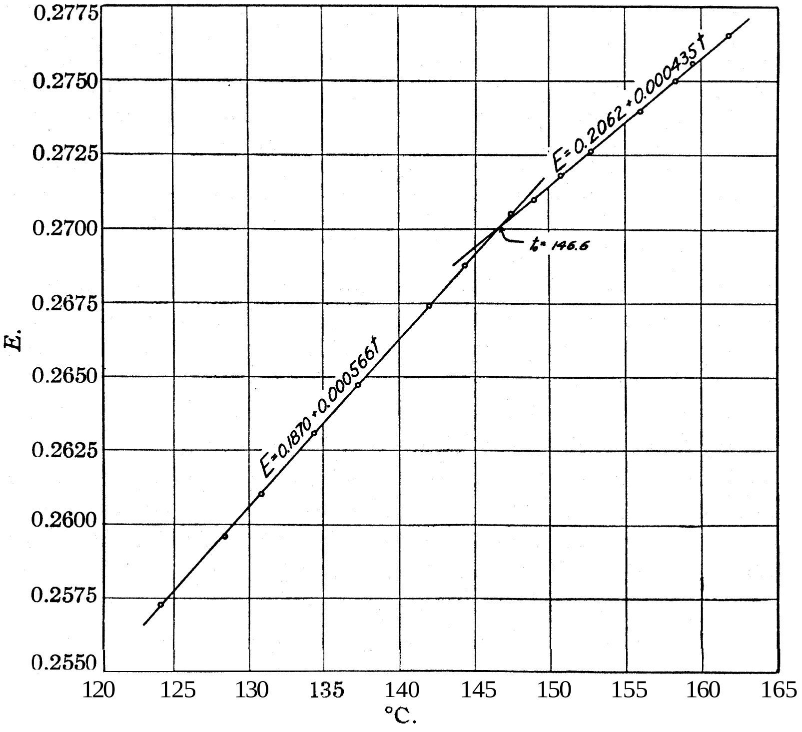

Fig. 2.

It may be seen that the temperature coefficient of e.m.f. is constant over two distinct ranges of temperature. The intersection of the two curves gives the transition temperature. To find this temperature accurately it was necessary to calculate the equation for each of the two curves, using the method of least squares, and to solve for the point of intersection. The equation of the lower curve, which we shall call the a-curve, since the a-form of silver iodide is stable in this range, is

$$E_1 = 0.1870 + 0.000566\,t \qquad (1)$$

The equation of the upper curve, which we shall designate as the P-curve, is

$$E_2 = 0.2062 + 0.000435\,t \qquad (2)$$

The intersection of these curves is found to be at 146.6°. This is the transition temperature of a- and β-silver iodide.

Table II shows the results obtained with Cell II. The asterisks indicate the points upon which calculations were based.

TABLE II

DATA FOR CELL II

t	E	t	E	t	E	t	E
115.90	0.2363	132.50	0.2440	146.90	0.2515	*155.80	0.2545
116.28	.2365	*133.10	.2444	147.60	.2518	155.30	.2543
116.70	.2368	134.12	.2448	*148.02	.2520	*154.50	.2540
117.32	.2370	134.68	.2451	148.70	.2523	154.20	.2538
118.10	.2373	135.95	.2458	149.30	.2525	*153.00	.2535
119.16	.2377	*136.43	.2460	150.40	.2528	*152.20	.2533
119.80	.2380	137.10	.2463	151.92	.2533	151.55	.2530
120.30	.2383	137.30	.2465	152.20	.2535	*150.60	.2526
120.69	.2385	138.00	.2468	153.00	.2538	150.35	.2525
121.38	.2388	*138.35	.2470	153.70	.2540	*149.45	.2522
121.67	.2390	139.30	.2473	154.60	.2543	*148.80	.2520
122.33	.2393	*139.80	.2476	155.30	.2545	147.85	.2518
122.80	.2395	140.56	.2480	156.13	.2548	147.05	.2515
123.98	.2400	141.10	.2483	156.55	.2550	146.90	.2510
124.72	.2403	141.40	.2485	156.98	.2551	146.55	.2513
*125.07	.2405	141.90	.2488	158.20	.2555	145.95	.2510
126.03	.2410	142.32	.2490	*158.80	.2558	145.48	.2508
126.71	.2413	142.90	.2493	159.55	.2560	144.50	.2500
127.02	.2415	*143.40	.2495	*160.30	.2562	143.68	.2497
127.70	.2418	143.89	.2498	161.00	.2564	142.50	.2492
128.62	.2422	144.30	.2500	159.80	.2560	141.80	.2483
*129.78	.2427	144.90	.2503	159.30	.2559	141.02	.2480
130.23	.2430	145.20	.2505	158.50	.2555	139.82	.2474
130.80	.2433	'145.70	.2508	157.95	.2553		
131.31	.2435	145.91	.2510	*157.00	.2550		
*132.00	.2438	146.50	.2513	156.55	.2548		

The equation of the a-curve, the one along which a-silver iodide is stable, is

$$E_1 = 0.1775 + 0.0005026\,t \qquad (3)$$

The equation of the β-curve is

$$E_2 = 0.1968 + 0.000371\,t \qquad (4)$$

The intersection of the two curves is found to be at 146.7°.

The transition temperature of silver iodide will be treated by us in a special paper. Suffice it to say here that the values mentioned in the earlier literature vary from 138 to 147°. This is a consequence of the strong retardations which may occur in this transition. In our case evidently there occurred no retardation, the electrolyte acting as an accelerator.

It is of interest to know the heat of transition of silver iodide. If we write this reaction, assumed to be occurring in the cell below the transition temperature, we have:

$$\mathrm{AgI}_\alpha + {}^1/_2\mathrm{Pb} = \mathrm{Ag} + {}^1/_2\mathrm{PbI_2} \qquad (5)$$

The reaction assumed to be occurring above the transition temperature is:

$${}^1/_2\mathrm{PbI_2} + \mathrm{Ag} = \mathrm{AgI}_\beta + {}^1/_2\mathrm{Pb} \qquad (6)$$

The summation of the two reactions gives

$$\mathrm{AgI}_\alpha = \mathrm{AgI}_\beta \qquad (7)$$

At the transition temperature, the two forms of silver iodide are in equilibrium, hence the free energy increases of the two reactions are equal, that is

$$\Delta F_5 = \Delta F_6 \qquad (8)$$

where the subnumerals refer to the marginal numbers of the equations. The increase in heat content for the transition as expressed by Equation (7) is given by the following equation

$$\Delta H_7 = TNf\left[\frac{dE_5}{dT} + \frac{dE_6}{dT}\right], \qquad (9)$$

where T is the temperature of transition on the absolute scale, N is the valence change, f is Faraday's constant and E is the electromotive force of the cell.

Let us now apply this equation to the data of Cell I. From (1) and (2)

$$\Delta H_7 = 419.6 \times 1 \times 96{,}500\ (0.000566 - 0.000435)$$
$$\Delta H_7 = 5304 \text{ joules} = 1267 \text{ cal. per gram mole}$$

The same calculation for Cell II (from 3 and 4) gives

$$\Delta H_7 = 419.7 \times 1 \times 96{,}500\ (0.0005026 - 0.000371)$$
$$\Delta H_7 = 5330 \text{ joules} = 1274 \text{ cal. per gram mole}$$

The average of these two values is 1270 cal., that is

$$\mathrm{AgI}_\alpha = \mathrm{AgI}_\beta - 1270 \text{ cal.}$$

Previous determinations by various investigators vary from 1355 to 1597 cal.

Summary

1. A type of transition cell pointed out by one of us many years ago, but hitherto never experimentally realized, has been constructed.

2. This transition cell of the sixth class, in which the depolarizer undergoes a polymorphic transformation, is experimentally realized in the case of silver iodide.

3. Temperature-e.m.f. measurements show the transition temperature to be 146.6°.

4. The heat absorbed during transition of one mole of AgI_α to one mole of AgI_β, calculated from the slopes of the e.m.f.-temperature curves, is 1270 cal.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

DECOMPOSITION OF DIACETONE ALCOHOL BY WEAKER BASES

BY GÖSTA ÅKERLÖF

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Introduction

In two preceding papers[1] have been given the results of the measurements of the decomposition velocity of diacetone alcohol in alkali hydroxide-alkali salt solutions. In this paper will be presented some measurements with weaker bases, such as ammonia, used as catalysts. Similar measurements for hydrogen ion catalysis with weaker acids present have been carried out by Harned and Hawkins[1c] for the hydrolysis of ethyl formate and ethyl acetate.

Previously it has been shown by Arrhenius,[2] Brönsted,[3] Harned[1] and others,[4] that when a neutral salt, which in itself is a strong electrolyte, is added to a solution of a weak electrolyte, the dissociation of this increases. For water as a weak electrolyte this increase has been measured by Harned[4a,b] Harned and Swindells,[5] Åkerlöf,[6] and Harned and James[7] for a number of different salt solutions. At low salt concentrations the curves obtained for the decomposition velocity of diacetone alcohol in neutral salt solutions of the weaker bases seemed to be of the same type as the curves obtained for the concentration of water as an electrolyte in the same salt solutions. In other words, the concentration of the weak bases as electrolytes was changed by the addition of neutral salts in the same manner as for water.

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[1] (a) Åkerlöf, THIS JOURNAL, 48, 3046 (1926); (b) 49, 2955 (1927); (c) Harned and Hawkins, *ibid.*, 50, 85 (1928). They give references relating to older literature on this subject.

[2] Arrhenius, *Z. physik. Chem.*, 31, 197 (1899).

[3] Brönsted, *J. Chem. Soc.*, 119, 574 (1921).

[4] (a) Harned, THIS JOURNAL, 47, 930 (1925); (b) *Z. physik. Chem.*, 117, 1 (1925); compare further (c) Schreiner, *Z. anorg. Chem.*, 135, 333 (1924); (d) Harned and Åkerlöf, *Physik. Z.*, 27, 411 (1926).

[5] Harned and Swindells, THIS JOURNAL, 48, 126 (1926).

[6] Åkerlöf, *ibid.*, 48, 1160 (1926).

[7] Harned and James, *J. Phys. Chem.*, 30, 1060 (1926).

The method proposed by **Harned** and **Hawkins** was used to calculate the concentration of the catalyzing ion and then from the mass action law the activity coefficients of the weak bases as electrolytes in their salt solutions. In agreement with the fundamental assumption made it was found that the curves for the activity coefficients came quite near each other. In many cases they seemed to superimpose well within the experimental uncertainties.

Experimental Methods and Materials

The weaker bases except ammonia were all obtained from the Eastman Kodak Company. Ammonia was redistilled from an alkali hydroxide solution with the usual precautions, but all the others were used without any attempt at further purification, due to well-known difficulties with small scale operations. An inquiry relative to the purity of the aliphatic amines used seemed to indicate that their purity was quite high. To judge from the methods used for their synthesis the amount of free ammonia present must in all cases have been very small. The bases were tested for the presence of carbonic acid and non-volatile matter. In a few cases slight traces were indicated but were considered as negligible. The method of measurement was the same as described in the preceding papers. In Table I are given some measurements for 0.2 N ammonia in sodium sulfate solutions.

TABLE I

SOME MEASUREMENTS WITH 0.2 *N* AMMONIA IN SODIUM SULFATE SOLUTIONS

Time, min.	1 *N* Na_2SO_4		2 *N* Na_2SO_4		3 N Na_2SO_4		4 N Na_2SO_4		5 *N* Na_2SO_4	
	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$
0	2.9	...	4.0	...	3.3	...	3.9	...	4.2	...
60	9.6	421	10.3	526	11.4	615	11.9	678	14.1	737
120	15.7	428	16.0	531	18.5	618	18.8	681	22.4	735
180	21.1	428	20.9	528	24.7	620	24.6	678	29.6	731
240	25.9	425	25.3	528	30.0	619	29.5	674	35.4	735
300	30.2	422	29.2	528	34.5	616	33.7	670	40.3	732
360	34.1	420	32.6	527	38.4	615	37.3	670	44.4	728
480	40.9	418	38.3	526	44.9	614	43.1	670	51.0	728
600	46.5	420	42.9	528	49.7	612	47.4	671	55.7	727
	73.5	...	59.3	...	64.7	...	59.2	...	67.6	...

It might be thought that the high volatility of the pure amines would cause errors due to their evaporation during the filling of the reaction tubes. The partial vapor pressure in 0.2 *N* pure aqueous solutions of some of the amines used may be estimated from a few measurements of Doyer[8] at 60° and those of Perman[9] for aqueous ammonia at varying temperature. Assuming proportionality in all cases, the following values

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[8] Doyer, *Z. physik. Chem.*, *6*, 486 (1890).

[9] Perman, *J. Chem. Soc.*, *[2]*83, 1168 (1903); Landolt-Börnstein, "Tabellen," 4th ed., p. 429.

in mm. of mercury are obtained: ammonia, 2.2; methylamine, 1.6; dimethylamine, 1.6; ethylamine, 2.6; diethylamine, 9.2. At least the order of magnitude is certain. When a salt is added the vapor pressure of water decreases and therefore that of the amine may increase. Let us assume that the partial vapor pressure of the latter has increased to 30 mm. of mercury and that the back pressure from the vacuum pump is 5 mm. The time used for filling the reaction tubes was about five minutes. The diameter of the capillary was around 0.08 cm. and the total length 90 cm. Applying the formula of Poiseuille for the flow of liquids through a capillary, we find that even under ideal conditions an almost negligible quantity (approximately 3%) of the amine as gas may pass through the capillary. However, the partial vapor pressure of the amine must rapidly decrease during the filling of the reaction tube because the evaporating surface decreases at about the same rate as the gas bubbles disappear. Therefore the amount of the amine actually lost must be far less than calculated for continuous equilibrium conditions. Differentiation of the mass action formula shows that a small error for the stoichiometrical concentration gives a very much smaller error for the hydroxyl ion concentration. In agreement herewith the velocity measurements appeared always to be very consistent.

TABLE II

SUMMARY OF THE MEASUREMENTS OF THE VELOCITY OF DECOMPOSITION FOR DIACETONE ALCOHOL IN 0.2 N SOLUTIONS OF WEAKER BASES

	Methylamine				Dimethylamine				Trimethylamine			
	NaCl		Na_2SO_4		NaCl		Na_2SO_4		NaCl		Na_2SO_4	
m_s	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0
0.00	458	1.00	458	1.00	240	1.00	240	1.00	62.5	1.00	62.5	1.00
.25	535	1.17	560	1.22	290	1.21	330	1.38	78.3	1.26	85.0	1.36
.50	559	1.22	609	1.33	312	1.30	375	1.56	86.7	1.39	100.2	1.61
.75	580	1.27	664	1.45	324	1.35	412	1.72	90.5	1.45	112	1.79
1.00	593	1.30	724	1.58	330	1.38	441	1.84	92.7	1.48	120	1.92
1.50	...	...	787	1.72	...	...	493	2.05	...	...	132	2.11
2.00	630	1.38	849	1.85	327	1.36	534	2.22	97.0	1.55	142	2.27
3.00	668	1.46	985	2.15	321	1.34	607	2.53	99.2	1.59	159	2.55
4.00	709	1.55	...	...	316	1.32	...	...	100.3	1.61	...	...
	Ethylamine[b]				Diethylamine				Triethylamine			
0.00	283	1.00	283	1.00	278	1.00	278	1.00	194	1.00	194	1.00
.25	325	1.15	354	1.25	330	1.19	358	1.29	241	1.24	258	1.33
.50	337	1.19	391	1.38	349	1.26	402	1.45	258	1.33	282	1.46
.75	351	1.24	421	1.49	355	1.28	431	1.55	269	1.39	297	1.53
1.00	360	1.27	456	1.61	359	1.29	456	1.64	280	1.44	313	1.61
1.50	...	...	499	1.76	...	...	492	1.77	...	...	325[c]	1.68
2.00	374	1.32	543	1.92	353	1.27	519	1.87	293[c]	1.51	...	...
3.00	388	1.37	625	2.21	347	1.25	560	2.02	...	...	...	...
4.00	396	1.40	...	...	341	1.23	583	2.10	...	...	...	...

TABLE II (Concluded)

	Ammonia				Tetramethylammonium hydroxide[d]		
	NaCl		Na_2SO_4		NaCl		
m_s	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	$K/K_0{}^e$
0.00	33.2	1.00	33.2	1.00	842	1.00	1.00
.25	38.5	1.16	49.5	1.49	...	...	...
.50	41.3	1.24	57.7	1.74	699	0.83	0.82
.75	42.5	1.28	64.0	1.93	...	...	...
1.00	43.0	1.30	70.5	2.13	626	0.74	0.71
1.50	...	...	79.0	2.38	...	...	...
2.00	40.7	1.23	88.0	2.65	530	0.63	0.58
3.00	36.6	1.10	103.0	3.10	445	0.53	0.48
4.00	33.5	1.01	112	3.37	396	0.47	0.44

[a] All K-values are to be multiplied by 10^{-5}.

[b] Due to unknown impurities in the ethylamine used, the velocity values found are probably all a little too small.

[c] The amine is partially salted out at higher salt concentrations.

[d] Tetramethylammonium hydroxide was used in 0.05 N solution.

[e] The values for K/K_0 with 0.1 N NaOH in NaCl solutions.

Experimental Results

The velocity measurements were carried out at 25° with the amines in sodium chloride or sulfate solutions. A summary of the results obtained is given in Table II. A few measurements with 0.05 N tetramethyl-

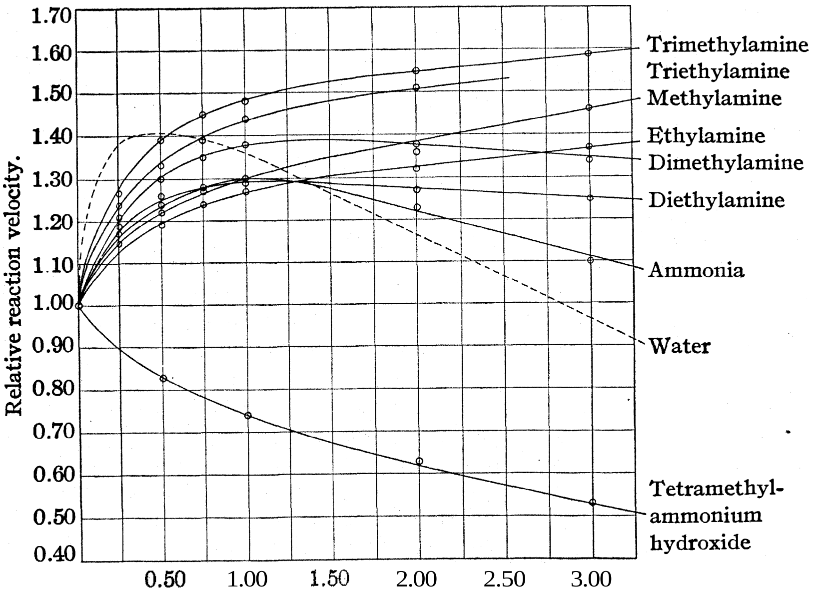

Fig. 1.—Curves for the relative decomposition velocity of diacetone alcohol in sodium chloride solutions of 0.2 N weaker bases.

ammonium hydroxide are also included. All salt concentrations m_s are given in weight normality. The amount of diacetone alcohol used was about 2% of the total volume of the solution. The velocity constants are given with the minute as unit of time. A graphical representation of the results is given in Fig. 1 for the amines in sodium chloride, in Fig. 2 in sodium sulfate solutions.

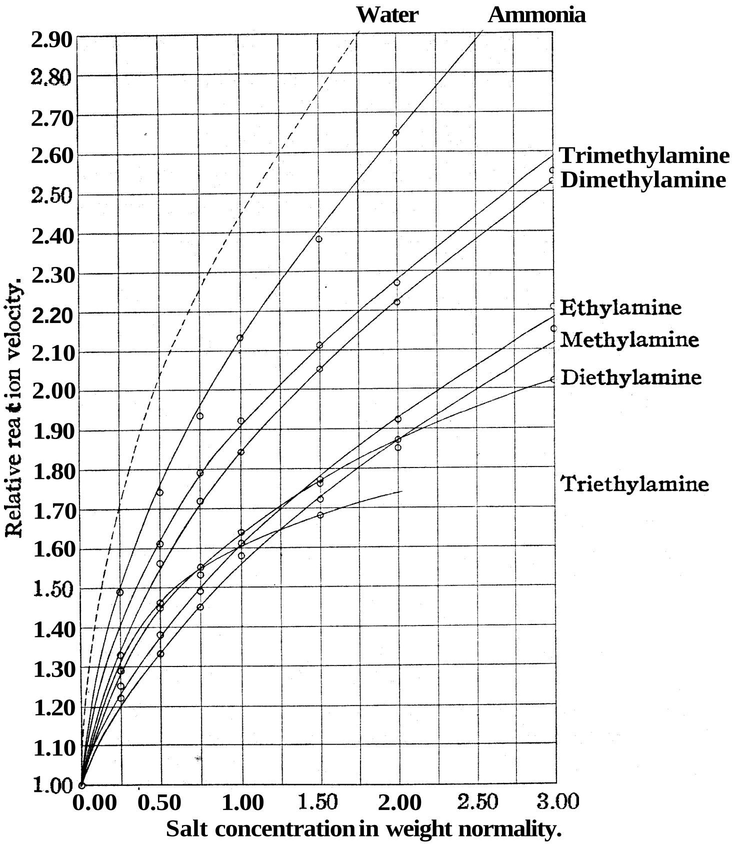

Fig. 2.—Curves for the relative decomposition velocity of diacetone alcohol in sodium sulfate solutions of 0.2 N weaker bases.

The Equilibrium Constants of the Weak Bases Used

The equilibrium constant k for the weak bases may be given by the following equation

$$k_{\mathrm{BOH}} = \frac{a_{\mathrm{B}} \cdot a_{\mathrm{OH}}}{a_{\mathrm{BOH}}} = \frac{\gamma_{\mathrm{B}} \cdot c_{\mathrm{B}} \cdot \gamma_{\mathrm{OH}} \cdot c_{\mathrm{OH}}}{\varphi_{\mathrm{BOH}} \cdot c_{\mathrm{BOH}}} = \frac{\gamma_{\mathrm{BOH}} \cdot c_{\mathrm{OH}}}{c_{\mathrm{BOH}}} \qquad (1)$$

where a denotes activities, γ ionic activity coefficients, c concentration and φ_{BOH} the activity coefficient of the non-electrolyte. The changes of φ_{BOH} may be relatively small. Therefore it may be assumed always to equal unity in pure aqueous solutions of the weaker **bases.** The equilibrium constants given in the literature are calculated without any reference to the changes of γ_{BOH}. At constant stoichiometrical concentration c we then obtain for the ratios between the equilibrium constants

$$k_1/k_2/k_3 \ldots = c_{OH(1)}/c_{OH(2)}/c_{OH(3)} \ldots \qquad (2)$$

The correction of c for c_{OH} is neglected because it is always comparatively small and the values of the equilibrium constants themselves seem many times to have appreciable errors. With the assumption of proportionality between hydroxyl ion concentration and reaction velocity, the following equation is obtained

$$\sqrt{k_1}/\sqrt{k_2}/\sqrt{k_3} \ldots = K_1/K_2/K_3 \ldots \qquad (3)$$

For ammonia the equilibrium constant seems to be known more accurately than for any other weak base. All the measurements were carried out by a conductivity method.[10] The curve for the changes of this constant for ammonia with varying temperature is shown in Fig. **3.** Interpolation gives for 25° the value $k = 1.85 \times 10^{-5}$. Table III summarizes

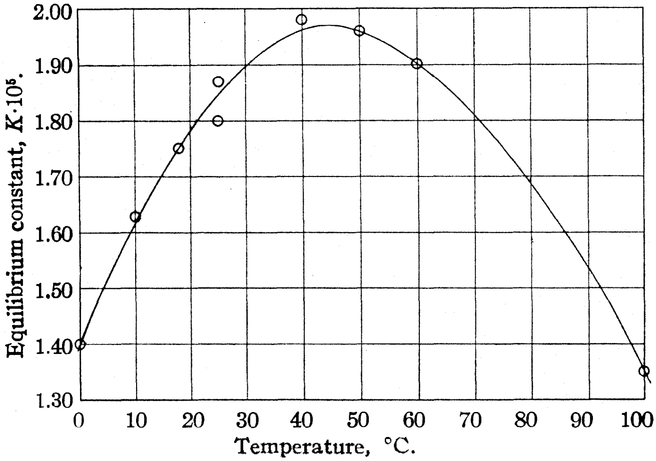

Fig. 3.—The equilibrium constant for ammonia at varying temperatures as obtained from conductivity measurements.

TABLE III

EQUILIBRIUM CONSTANT FOR AMMONIA AS CALCULATED FROM VELOCITY MEASUREMENTS

Base	k	$K \times 10^5$	k for ammonia
Dimethylamine	7.4×10^{-4}	240	1.42×10^{-5}
Trimethylamine	7.4×10^{-5}	62.5	2.09×10^{-5}
Diethylamine	1.3×10^{-3}	278	1.85×10^{-5}
Triethylamine	6.4×10^{-4}	194	1.88×10^{-5}
Ammonia	......	33.2	Mean 1.81×10^{-5}

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[10] (a) Lunden, J. *chim. phys.*, *5*, *574* (1907); (b) Kanolt, THIS JOURNAL, 29, 1408 (1907); (c) Noyes, Kato and Sosman, *Z. physik. Chem.*, *73*, 1 (1910); (d) Landolt-Börnstein, "Tabellen," 4th ed., p. 1133.

the calculations of the value of this constant as obtained from the velocity measurements. The equilibrium constants used were measured by Bredig.[11] The mean value is only a little lower than the one obtained from the conductivity measurements but the agreement may seem to be rather accidental. It might seem to be possible to test the value for the equilibrium constant in another way. Assume that the proportionality factor between reaction velocity and mean activity of the base used is the same for a weak one as for a strong one. For 0.1 *N* sodium hydroxide the activity coefficient is $\gamma_{NaOH} = 0.767$ and the reaction velocity for the decomposition of diacetone alcohol $K = 0.0208$. With the equilibrium constant for ammonia $k = 1.85 \times 10^{-5}$ and the activity of the hydroxyl ion corrected according to the limiting function of Debye and Hiickel, the calculation gives for 0.2 N solution $K = 49.2 \times 10^{-5}$ as against the measured value $K = 33.2 \times 10^{-5}$. At least the order of magnitude is the same for both values. The discrepancy seemed, however, to be too large and therefore the velocity value for the pure ammonia solution was remeasured with the greatest care. A slightly higher value was found but the difference from the previous value was so small that a correction was considered unnecessary.

For 0.2 N ammonia we may therefore accept the equilibrium constant $k = 1.85 \times 10^{-5}$ and the reaction velocity for the decomposition of diacetone alcohol $K = 33.2 \times 10^{-5}$. A summary of the calculations of the equilibrium constants for the other weak bases used from the velocity measurements with these reference values is given in Table IV.

TABLE IV

EQUILIBRIUM CONSTANTS CALCULATED FROM THE VELOCITY MEASUREMENTS

Base	$K \times 10^5$	k	k (Bredig)
Methylamine	458	3.5×10^{-3}	5.0×10^{-4}
Dimethylamine	240	9.7×10^{-4}	7.4×10^{-4}
Trimethylamine	62.5	6.5×10^{-5}	7.4×10^{-5}
Ethylamine	283	1.3×10^{-3}	5.6×10^{-4}
Diethylamine	278	1.3×10^{-3}	1.3×10^{-3}
Triethylamine	194	6.3×10^{-4}	6.4×10^{-4}
Ammonia	33.2[a]	1.85×10^{-5}[a]	.....

[a] Reference values.

The k-values obtained for the weakest bases agree fairly well with the values measured by Bredig. The strongest bases are gases at ordinary temperatures and far more difficult to purify than the weaker ones. Since any impurity like free ammonia apparently must lower their k-values, it is believed, that our values are nearer the true ones than those previously given in the literature. The reaction velocity and k-value for ethplamine are probably a little too small.

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[11] Bredig, *Z. physik. Chem.*, **13**, 289 (1894).

Activity Coefficients of the Weak Bases as Electrolytes in Sodium Chloride and Sulfate Solutions

In the preceding paper it was shown that the decomposition velocity for diacetone alcohol in pure aqueous solutions of the alkali hydroxides was proportional to their mean activity

$$K_{\mathrm{MeOH}} = R\cdot\gamma_{\mathrm{MeOH}}\cdot m_{\mathrm{MeOH}} \qquad (4)$$

where R is the proportionality factor. For alkali hydroxide-salt solutions this simple formula cannot be applied but the reaction velocity may be expressed by the following equation

$$K_{\mathrm{MeOH(S)}} = R\cdot m_{\mathrm{MeOH}}\cdot F(x) \qquad (5)$$

where (S) indicates an hydroxide-salt solution and $F(x)$ is a complex unknown factor. If we exchange the alkali hydroxide in the salt solutions against a weak base, the activity coefficient of the hydroxyl ion must remain nearly constant, because it is given by the nature of the environment, which remains nearly constant. The reaction velocity in the weak base-salt solution may then be expressed by a formula similar to (5)

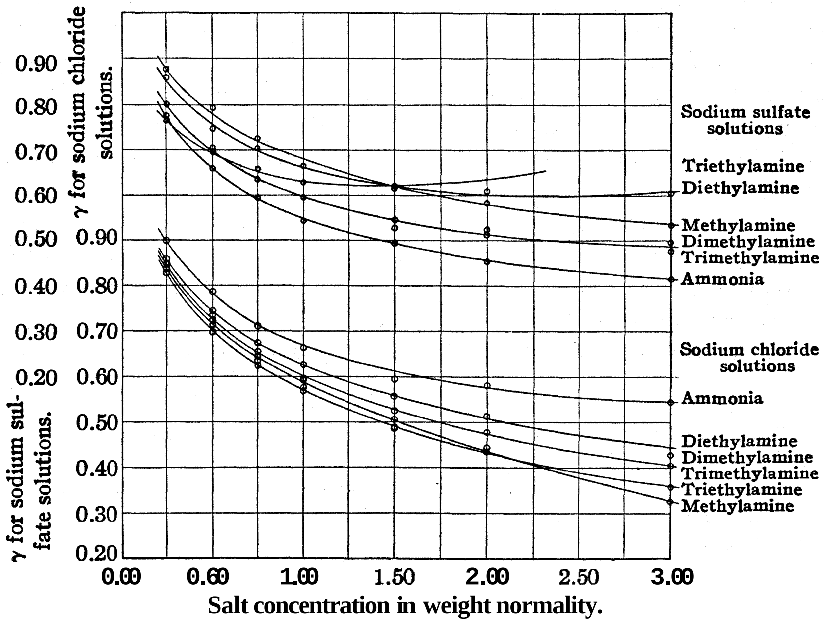

Fig. 4.—Curves for the mean activity coefficients of the weaker bases as electrolytes in sodium chloride and sulfate solutions calculated with the velocity measurements for 0.1 N sodium hydroxide in the same salt solutions.

$$K_{\mathrm{BOH(S)}} = R\cdot m_{\mathrm{OH(BOH)}}\cdot F(x) \qquad (6)$$

Assuming complete dissociation of the hydroxide, division of (5) by (6) gives

$$K_{\mathrm{MeOH(S)}}/K_{\mathrm{BOH(S)}} = m_{\mathrm{MeOH}}/m_{\mathrm{OH(BOH)}} \qquad (7)$$

From this equation we may calculate $m_{\mathrm{OH(BOH)}}$, when all other variables are known. Harned and Hawkins used the same method for calculating the hydrogen-ion concentration in weak acid-salt solutions. With the knowledge of $m_{OH(BOH)}$ we may use the mass action law to obtain γ_{BOH} on the assumption that φ_{BOH} (Equation 1) always equals unity. The magnitude of φ_{BOH} is connected with the salting out effect on the amines. At present we will disregard the influence of this factor in order to see whether we get reasonable values for the ionic activity coefficients of the weak bases without it. In Table V is given a summary of the calculated mean activity coefficients of the weak bases as electrolytes in sodium chloride and sulfate solutions. The curves for the mean activity coefficients are given in Fig. 4.

TABLE V

MEAN ACTIVITY COEFFICIENTS OF THE WEAKER BASES AS ELECTROLYTES IN SODIUM CHLORIDE AND SULFATE SOLUTIONS

		A. Methyl		B. Dimethyl		C. Trimethyl		D. Diethyl	
m_c	K_{NaOH}	K_{BOH}	γ_{BOH}	K_{BOH}	γ_{BOH}	K_{BOH}	γ_{BOH}	K_{BOH}	γ_{BOH}
0.25	184	53.5	0.84	29.0	0.85	7.83	0.84	33.0	0.86
.50	170	55.9	.74	31.2	.72	8.67	.70	34.9	.74
.75	158	58.0	.65	32 4	.64	9.05	.62	35.5	.68
1.00	149	59 3	.59	33.0	.59	9.27	.57	35.9	.63
1.50	133	61.0	.51	33.1	.52	9.57	.48	35.8	.56
2.00	121	63.0	.44	32.7	.48	9.70	.44	35.3	.51
3.00	101	66.8	.33	32.1	.40	9.92	.36	34.7	.43
4.00	91.8	70.9	.27	31 6	.37	10.03	.32	34.1	.39
		G. Methyl		H. Dimethyl		E. Triethyl		P. Ammonia	
0.25	200	56.0	0 8 8	33.0	0.80	24.1	0.83	3.92	0.90
.50	199	60.9	.80	37.5	.70	25.8	.71	4.13	.79
.75	199	66.4	.72	41.2	.64	26.9	.63	4.25	.71
1.00	200	72.4	.66	44.1	.59	28.0	.57	4.30	.66
1.50	204	78.7	.62	49.3	.53	29 0	.49	4.27	.59
2.00	210	84.9	.58	53.4	.51	29.3	.44	4.07	.58
3.00	224	98.5	.53	60.7	.48	...	...	3.66	.55
4.00	...	...	...	....	...	...	...	3.35	.54
		I. Trimethyl		K. Diethyl		L. Triethyl		M. Ammonia	
0.25	200	8.50	0.84	35.8	0.86	25.8	0.76	4.95	0.77
.50	199	10.02	.71	40.2	.75	28.2	.69	5.77	.66
.75	199	11.2	.63	43.1	.70	29.7	.66	6.40	.59
1.00	200	12.0	.59	45.6	.67	31.3	.63	7.05	.54
1.50	204	13.2	.55	49.2	.63	32.5	.61	7.90	.49
2.00	210	14.2	.52	51.9	61	...	...	8.80	.45
3.00	224	15.9	.50	56.0	.60	...	...	10.30	.41

A–F, values for sodium chloride; G M, values for sodium sulfate solutions. All reaction velocities to be multiplied by 10^{-4}.

Discussion of the Results

The values for the mean activity coefficients of the weaker bases as electrolytes given in Table V were calculated without any consideration that the values used for the reaction velocities did not refer to solutions of the same total ionic strength. Due to the approximate nature of the calculations, a correction seems to be unnecessary. It would cause only very slight changes for the values of the mean activity coefficients.

The curves for these activity coefficients in Fig. 4 show that for a given salt concentration values of the same magnitude were obtained for all the weaker bases used. Several curves superimpose on other curves in their entire length. For some of them where this is not the case, it seems as if they were superimposable within the experimental errors. In accordance with the assumption made for the method of calculation used this could be expected.

So far the results seem to be reasonable. However, at small salt concentrations the slope of the curves seems to be too small. In other words, the values obtained may be too high. There are no other electrolytes found with such high values for the mean activity coefficients in dilute solutions. On the contrary, we would expect these amines to have quite small activity coefficients in salt solutions on account of the complexity of their ions. In this case the addition of a small amount of salt would have caused a very sharp decrease for their activity coefficients.

It seems to be out of the question that the measurements themselves could have such large errors that they gave a distorted view of the calculations. The assumption of incomplete dissociation of the alkali hydroxide in hydroxide-salt solutions would give an increase for the activity coefficients and therefore cannot be considered. The salting out effect on the amines increases the value of φ_{BOH} and as we calculated the hydroxyl ion concentration without any assumption regarding this effect we have instead multiplied the activity coefficients with the increase in this factor. The increase must, however, be small even in fairly concentrated salt solutions, as might be concluded from the measurements with triethylamine.

It was shown above that the value for the decomposition velocity of diacetone alcohol in 0.2 N ammonia as calculated from the equilibrium constant and the velocity in 0.1 N sodium hydroxide ($49.2 \cdot 10^{-5}$) did not agree with the measured one ($33.2 \cdot 10^{-5}$). The proportionality factor for reaction velocity and ionic activity must have changed from the strong base to the weak one in the ratio of these two values. Harned and Hawkins found that the same proportionality factor could be used for strong as well as weak acids. A reason for the difference might be found in the difference in behavior the reactions used show towards the properties of the catalysts. Harned and Pfanstiel[12] have found it probable that the velocity of hydrolysis of ethyl acetate in solutions of hydrochloric acid is proportional to the activity of the hydrogen ion. For the decom-

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[12] Harned and Pfanstiel, THIS JOURNAL, 44, 2193 (1922).

position of diacetone alcohol in alkali hydroxide solutions the measurements seem to indicate that the velocity is proportional to the mean activity of the hydroxides. If then the cation present is exchanged against another one of different character it might be reasonable to expect a change also for the proportionality factor.

In Table VI are given some values for the mean activity coefficients of the weaker bases corrected for the change in proportionality factor from the alkali hydroxides to the weaker bases. There is also given a comparison between these corrected values and those derived from the measurements with tetramethylammonium hydroxide in sodium chloride solutions. The cation of this base must stand far nearer the cations of the weak bases than the alkali metal ions. In Fig. 5 are shown curves for the corrected and uncorrected values, a curve for values calculated from the measurements with tetramethylammonium hydroxide and the corresponding curves obtained by Harned and Hawkins for weak acids in sodium chloride solutions. Tetramethylammonium hydroxide apparently belongs to the strong bases, but it is considerably weaker than any one of the alkali hydroxides. The mean activity coefficients of the weaker bases obtained with the measurements for solutions of this hydroxide come between the corrected and uncorrected values given in Table VI.

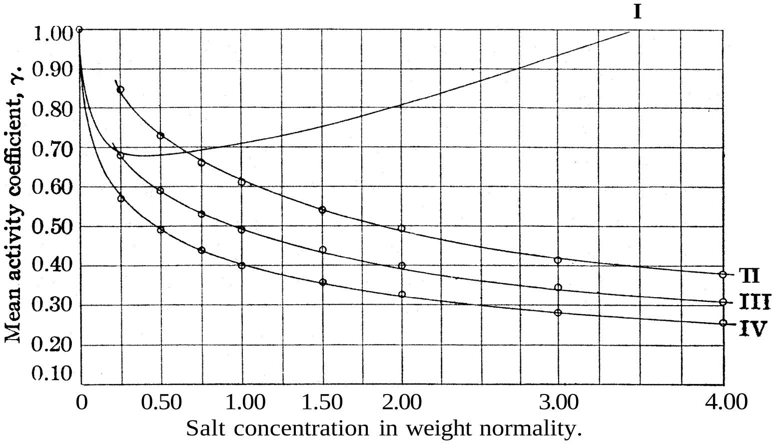

Fig. 5.—Comparison of the curves for the mean activity coefficients of the weaker bases as electrolytes in sodium chloride and sulfate solutions calculated:

I, with velocity measurements for 0.1 N sodium hydroxide (Curve II for dimethyl- or diethylamine in NaCl solutions); II, with velocity measurements for 0.05 N tetramethylammonium hydroxide (Curve III for dimethyl- and diethylamine in NaCl solutions); III, with corrected proportionality factor (Curve IV for dimethyl- and diethylamine in NaCl solutions); Curve I gives the activity coefficient for mono- or dichloro-acetic acid in sodium chloride solutions.

The corrected values seem to be of a reasonable magnitude with regard to the measurements of Harned and Hawkins. As was expected, quite small mean activity coefficients are obtained at high salt concentrations.

TABLE VI

CORRECTED MEAN ACTIVITY COEFFICIENTS FOR THE WEAKER BASES AS ELECTROLYTES IN SODIUM CHLORIDE AND SULFATE SOLUTIONS

	Methylamine			Dimethylamine			Trimethylamine		
m_s	I[a]	II[b]	III[c]	I[a]	II[b]	III[c]	I[a]	II[b]	III[c]
0.25	0.84	0.67	0.56	0.85	0.68	0.57	0.84	066	0.57
.50	.74	.59	.49	.72	.59	.49	.70	.58	.47
.75	.65	.52	.44	.64	.53	.43	.62	.51	.42
1.00	.59	.49	.40	.59	.49	.40	.57	.48	.38
1.50	.51	.42	.34	.52	.44	.35	.48	.42	.32
2.00	.44	.37	.29	.48	.40	.32	.44	.38	.30
3.00	.33	.28	.22	.40	.35	.27	.36	.31	.24
4.00	.27	.22	.18	.37	.31	.25	.32	.28	.22
	D[d]	E	F	G	H	I	K	L	M
0.25	0.58	0.56	0.60	0.59	0.54	0.56	0.58	0.51	0.52
.50	.50	.48	.53	.54	.47	.47	.50	.47	.44
.75	.45	.42	.48	.49	.43	.42	.47	.44	.40
1.00	.42	.38	.44	.45	.40	.40	.45	.42	.36
1.50	.37	.33	.40	.41	.36	.37	.42	.41	.33
2.00	.34	.29	.39	.39	.34	.35	.41	...	.30
3.00	.29	...	.37	.36	.32	.33	.40	...	.28

[a] Uncorrected values given in Table V for sodium chloride solutions.

[b] Values calculated from measurements with 0.05 N tetramethylammonium hydroxide in sodium chloride solutions.

[c] Values calculated with corrected proportionality factor.

[d] The letters D, E, F, etc., refer to those for the amines in Table V. All values are corrected.

Summary

Measurements of the decomposition velocity of diacetone alcohol in sodium chloride and sulfate solutions of weak bases are presented. A discussion of the equilibrium constants of the weak bases used has been given. The values found for the strongest bases are probably more accurate than values previously given in the literature.

The activity coefficients of the weaker bases as electrolytes in salt solutions cannot be calculated on the assumption that a weak base has the same proportionality factor between activity of the base and reaction velocity as a strong one. A correction factor for the activity coefficients was calculated from the reaction velocities measured in pure aqueous solutions of 0.1 N sodium hydroxide and one of the amines.

The corrected mean activity coefficients seem to have reasonable values. The decrease in dilute salt solutions is of the same magnitude as found by Harned and Hawkins for weak acids in the same salt solutions.

PHILADELPHIA, PENNSYLVANIA

THE SYNTHESIS OF AMMONIA BY ALPHA RAYS[1]

BY S. C. LIND AND D. C. BARDWELL

RECEIVED DECEMBER 14, 1927 PUBLISHED MARCH 7, 1928

Owing to the general interest in active nitrogen and the various efforts to learn something of its nature by means of its reactivity towards hydrogen and other reagents, the writers decided to reëxamine the behavior of a mixture of hydrogen and nitrogen under a radiation of radon.

Earlier experiments were made in a stagnant system by Cameron and Ramsay[2] who mixed hydrogen, nitrogen and radon in a volume of 2.3 cc. and judged the rate of ammonia synthesis from the resulting fall in pressure. From their results Lind[3] calculated the ion yield to be $+M_{NH_3}/-N_{(N_2 + H_2)} = 0.12$ or about 8 ion pairs for 1 molecule of ammonia formed. Later, Usher[4] repeated the experiments of Cameron and Ramsay with refinements. While he confirmed a reduction in pressure, he could find no very certain amounts of ammonia (less than 1% of that required by the pressure change) and attributed the decrease of pressure largely to a loss of hydrogen in the glass wall, which he in fact recovered by heating, together with a much smaller amount of nitrogen.

In the present experiments the writers employ the method of streaming a mixture of hydrogen and nitrogen past a thin a-ray bulb containing radon and later titrate the ammonia after direct absorption in water or in acid. Thus we avoid the disadvantages of a system of small volume.

Fortunately the stoichiometric mixture of highly purified hydrogen and nitrogen used in the Fixed Nitrogen Research Laboratory for catalytic synthesis of ammonia was at our disposal. This was passed at the rate of 50 cc. per minute under ordinary pressure through a glass sphere (625 cc. volume; 10.6 cm. diameter) at the center of which was mounted a thin a-ray bulb (1.4 mm. diameter; about 5μ wall thickness). The system is essentially that originally used for ozone synthesis[5] with some modification, as in later work,[6] of the method of sealing in the a-ray bulb and of retaining the radon in it.

Preliminary qualitative tests with Nessler reagent proved the production of ammonia. The quantitative titrating agents were 0.01 N sulfuric acid and 0.01 N potassium hydroxide solutions. Sodium alizarin sulfate

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[1] This work, which was carried out in the Fixed Nitrogen Research Laboratory at Washington, was the subject of a preliminary report at a Regional Meeting of the Society in Chicago, May, 1927.

[2] Cameron and Ramsay, *J. Chem. Soc.*, 93, 988 (1908).

[3] Lind, *J. Phys. Chem.*, 16, 581 (1912).

[4] Usher, *J. Chem. Soc.*, 97, 389–405 (1910).

[5] Lind, *Am. Chem. J.*, 47, 397 (1911); *Sitzb. Akad. Wiss. Wien*, 120, 1709 (1911).

[6] Lind and Bardwell, THIS JOURNAL, 45, 2586 (1923).

was used as indicator,' the end-point always being reached from the alkaline side.

The **ionization** during an interval of reaction was calculated as follows. N ion pairs = millicuries of radon (measured in place by the γ-ray method) X total number of a-rays from 1 millicurie of Rn + RaA + RaC (= 3 X 1.772 X 10^{13}) X intensity of ionization per cm. of path per 1 a-ray for air N. T. P. in the system used, estimated as (3 X 10^4), X spec. ionization of $3H_2 + N_2$ mixture (= 0.41 when air = 1) $\times$ actual path in cm. (= (10.6 – 0.14)/2) X $273/(273 + t)$ X $P/760$ (when P = mean of initial and final pressures of any interval).

The data are shown in Table I.

TABLE I

YIELD OF AMMONIA PER ION PAIR

Reaction $3H_2 + N_2 = 2NH_3$ in a flow system with a-ray bulb. Flow = 50 cc. per minute. E_0 = 96.2 m.c. Rn. Temp. = 25°.

April, 1926 init. time	Interval. hours	Radon decayed	Bar., mm.	Cc. of 0.01 N H_2SO_4	Moles NH_3 X 10^{18}	Ion pairs $\times$ 10^{18}	$\frac{M_{NH_3}}{N_{ions}}$	Absorbent
2 P.M., 4/23	4	2.84	742	0.40	2.4	8.7.1	0.276	Water'
6 P.M., 4/23	4	2.76	742	.37	2.2	8.4	.262	Water
10 P.M., 4/23	10.5	6.86	742	.65	3.9	21.0	.186	Water
9 A.M., 4/24	13.3	7.90	750	.73	4.4	24.0	.183	Water
10:20 P.M., 4/24	17.7	9.35	754	.80	4.8	29.0	.165	Water
4:10 P.M., 4/25	16.2	7.53	749	.63	3.8	23.3	.167	Water
8:30 A.M., 4/26	24.0	9.66	754	.78	4.7	30.2	.155	Water
8:30 A.M., 4/27	25.5	8.50	747	.90	5.4	26.4	.204	Acid[b]
10:15 A.M., 4/28	46.2	11.8	748	1.25	7.5	36.7	.205	Acid[c]

[a] About 75 *cc.* in a multi-bubble absorption flask.

[b] 0.5 cc. of 0.01 N H_2SO_4 in about 75 cc. of water.

[c] 1.0 cc. of 0.01 N H_2SO_4 in about 75 cc. of water.

Discussion of Results

From Table I (next to last column) one sees that there is a distinct synthesis of ammonia in an a-ray flow system. The yield is much higher than found by Usher[4] and nearly twice as high as reported by Cameron and Ramsay[2]—both in small volumes of stagnant gas.

As long as water was used as absorbent liquid, the yield recovered per ion pair fell steadily as the concentration of ammonia in the total gas diminished due to the decay of the radon. This suggests incomplete absorption. Although absorption in water is the standard method used in testing ammonia catalysts, our concentration is of much lower order, one part in 10^5 to 10^6 as against parts per 10^2 in catalysis. In the last two experiments some initial acid (not a final excess) was added to the water to obtain better retention of ammonia. The recovered yield was

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[7] Cohn, "Indicators and Test Papers," John Wiley and Sons, Inc., New York, 1902, p. 25.

increased and remained constant at 0.205, which is, however, considerably below the initial 0.276 in water, so that some doubt must remain as to the exact yield, which could only be settled by more elaborate experiments on absorption at low concentration. The yield appears to lie between 0.2 and 0.3 molecule of ammonia per ion pair.

From such a low ionic efficiency, relative to most other reactions that have been examined under α-radiation,[8] it is difficult to judge whether the ions of either reactant are directly responsible for the reaction. In a mixture of $3H_2:1N_2$ about 60% of the ionization produced by a-rays falls on the N_2 and 40% on the H_2, so that referring all the reaction to either set of ions would not raise the yield to a value that would aid in the decision. Furthermore, such reasoning loses its point if we accept the recent evidence of Harnwell[9] and others that positive ions capture electrons from molecules of lower ionization potential so that all of the ionization is transferred to one species of molecules. If it means that both components must be ionized (or activated) it is an interesting analogy with the recent result of Lewis[10] that it is necessary to activate bath nitrogen (Strutt's method) and hydrogen (Wood's method) in order to synthesize ammonia by such means.

Equilibrium under a-Radiation

Although it is not the purpose of this paper to discuss the equilibrium of the reaction, one or two simple deductions will be made.

According to Wourtzel[11] the rate of decomposition of NH_3 by a-rays at 25° is approximately $-M_{NH_3}/N_{NH_3} = 1$, which has been confirmed by Lind and Bardwell.[12] If we take the rate of synthesis as $+M_{NH_3}/N_{(H_2 + N_2)} = 0.2$, then equilibrium as predicted on simplest assumptions from the two opposed rates should be realized in a mixture when 5 times as much ionization falls on the $3H_2 + N_2$ molecules as on the NH_3 molecules. Taking the specific molecular ionization of $3H_2 + N_2$ as 0.41 and that of NH_3 as 0.82, equilibrium should occur when 83.3% of initial NH_3 has been decomposed, that is, in 10 volumes of stoichiometric mixture to 1 volume of ammonia, or a mixture containing 9.09% of NH_3 by volume. No direct test of this prediction has been made. Since Usher found very little synthesis in a static system he concluded that equilibrium would lie almost entirely on the decomposition side. This conclusion is not supported by the present results on synthesis and is also at variance with the indications of the kinetic course of the decomposition. Application

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[8] Lind, "Chemical Effects of α Particles," 2nd ed., Chemical Catalog Co., New York, 1928, pp. 100–103.

[9] Harnwell, *Phys. Rev.*, 29, 683 (1927); 29, 830 (1927).

[10] Bernard Lewis, THIS JOURNAL, 50, 27 (1928).

[11] Wourtzel, *Le Radium*, 11, 342 (1918).

[12] Unpublished results.

of the general equation to Usher's data for decomposition[13] to 57%, showed that the velocity constant falls steadily as the reaction proceeds, as if due to reverse reaction. The results of Lind and Bardwell,[12] in which decomposition proceeded to 73%, show a similar and more far-reaching drop with some indication that the yield in synthesis is somewhat nearer 0.3 than 0.2 molecule per ion pair.

Summary

Using a method of flowing a stoichiometric mixture of hydrogen and nitrogen past an a-ray bulb, the rate of ammonia synthesis found by chemical titration is estimated to be 0.2 to 0.3 molecule per ion pair produced in the mixture, a yield higher than previously found in stagnant gases for this reaction but low in comparison with the majority of gas reactions under a-radiation. This yield in synthesis is in general accord with the observed fall of velocity constant in decomposition of ammonia by a-rays as a function of the ammonia concentration.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 43]

AN INVESTIGATION OF THE REACTION OF SODIUM ALIZARIN MONO-SULFONATE WITH ALUMINUM UNDER DIFFERENT EXPERIMENTAL CONDITIONS WITH REFERENCE TO ITS USE IN COLORIMETRY

BY JOHN H. YOE AND WILLIAM L. HILL

RECEIVED DECEMBER 19, 1927 PUBLISHED MARCH 7, 1928

A method for the colorimetric determination of aluminum has been reported by Atack,[1] in which the principal reagent is sodium alizarin mono-sulfonate (Alizarin Red S). With aluminum in alkaline solution this dye forms a red lake which is fairly stable in the presence of a considerable excess of acetic acid.

> "The original solution (5 to 20 cc.) is acidified with hydrochloric acid or sulfuric acid, as acetic acid would form the highly dissociated aluminum acetate, and this has been found to give a somewhat more intense coloration than the inorganic salts; nitric acid in considerable amounts leads to the partial destruction of the coloration. Ten cc. of glycerine and 5 cc. of a 1% solution of Alizarin S are added, the solution made up to about 40 cc. with water, and then rendered slightly ammoniacal. After standing for five minutes it is acidified with dilute acetic acid, the Alizarin S acting as an indicator, acetic acid being added until no further change in the coloration occurs. The liquid is then made up to 50 cc. and compared with a standard."

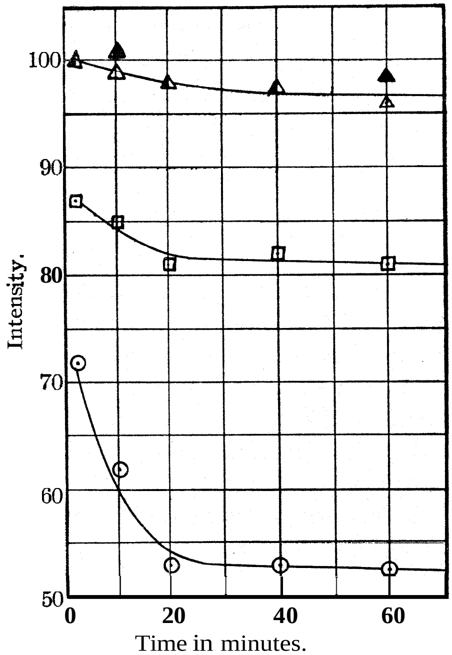
Commenting upon this procedure, Atack states in substance:

[13] Lind, *J. Phys. Chem.*, 16, 595 (1912).

[1] Atack, *J. Soc. Chem. Ind.*, 34, 936 (1915).

(1) A very large excess of the dye is necessary, but its original color in acid solution is not of sufficient intensity to interfere with the test. **(2)** Moderate amounts of calcium, magnesium or zinc salts do not affect the final color intensity. **(3)** Large quantities of iron and chromium salts and of phosphates interfere with the test. (4) The interference of iron and chromium may be prevented by the addition of a citrate before adding the ammonium hydroxide. Thus, the coloration given by **0.015** mg. of aluminum was not affected by **10** mg. of iron. (5) Since acetic acid slowly attacks the aluminum lake, especially in the presence of phosphates, the comparisons must be made within a short time. (6) The temperature at which the lake is formed does not affect the final color, if the acetic acid is added in the cold. (7) The glycerine prevents precipitation, which takes place readily in the presence of salts of other metals. (8) One part of aluminum in 10 million parts of water can be detected readily; suitable amounts for estimation are **0.005** to **0.05** mg.

The purpose of this paper is to present some specific data on the effects of varying the several factors in the procedure outlined above. The apparatus, method of attack and general procedure have been described in detail in a recent paper by Yoe and Hill.[2]



△, **0.1%** of dye, **5** cc. of HAc in light; ▲, 0.1% of dye, 5 cc. of HAc in dark; ⊡, 0.1% of dye, 5 cc. of HAc and 10 cc. of glycerine; O, 0.1% of dye, **10** cc. of HAc.

Fig. 1.—"Aging."

Experimental

Reagents.—1. Acetic acid, 5 N. 2. Hydrochloric acid, 1 N. **3.** Ammonium hydroxide, 5 *N*. 4. Ammonium citrate, 5 N. 5. Standard aluminum chloride solution; 1 cc. contained 0.10 mg. of aluminum. For method of preparation and standardization, see ref. 2. 6. Solutions of the several salts used in the study of the effects of ions were prepared so that 1 cc. would contain 10 mg. of the desired ion if the salt were completely dissociated. In the study of positive ions chlorides were used, in all other cases sodium salts were employed. 7. Alizarin S solution. Four grams of Alizarin Red S, Schultz No. 780, National Aniline and Chemical Co., Inc., New York, N. Y., was dissolved in distilled water, filtered from the small amount of sediment and made up to a volume of 400 cc. This 1% stock solution was diluted to 0.1% and 0.2% solutions as needed. 8. Glycerine, clear white.

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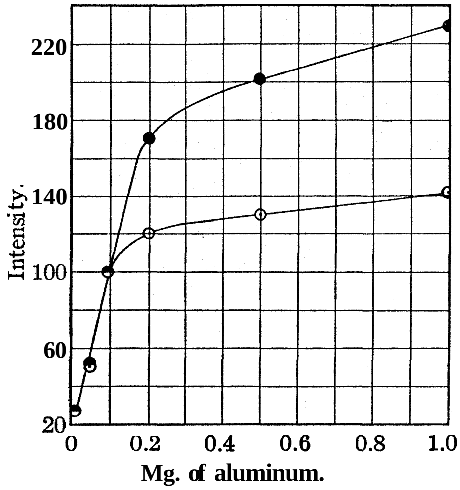
[2] Yoe and Hill, THIS JOURNAL, 49,2395 (1927).

Procedure.—The order of addition of the reagents, as well as the quantities added, unless otherwise stated, was as follows. To 1 mg. of aluminum in a Nessler tube were added 5 cc. of 1 N hydrochloric acid, 5 cc. of a 0.1% Alizarin S solution and sufficient distilled water to bring the volume to 30 cc. Then 2 cc. of 5 N ammonium hydroxide was added with gentle stirring and after standing for five minutes 5 cc. of 5 N acetic acid was put in and mixed thoroughly. The solution was then diluted to 50 cc., thoroughly mixed and allowed to stand in the Nessler tube until time for comparison. In all instances where glycerine was employed it was added just after the hydrochloric acid and thoroughly mixed. Unless otherwise stated the temperature was 23°.



⊙, with 0.1% of dye; ■, with 0.2% of dye.

Fig. 2.—Concentration of aluminum.

"Aging."—In Fig. 1 the curves show the decrease in color intensity with time after the addition of acetic acid, both in the light and in the dark, for different concentrations of acetic acid, and also when 10 cc. of glycerine was added. The intensities for each curve have been expressed in terms of the two minute intensity with 5 cc. of acetic acid and "aged" in the light.

Effects of Varying the Quantities of the Reagents.—The quantities of the reagents were varied one at a time, all other conditions being kept constant. All solutions were "aged" for twenty-five minutes and the intensities are expressed in terms of the intensity of the standard at the end of twenty-five minutes. The results are shown in Figs. 2, 3 and 4, and in Table I.

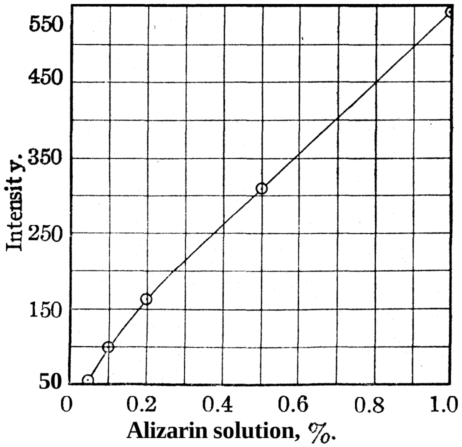


Fig. 3.—Concentration of Alizarin S.

Conditions During Lake Formation.—In Figs. 5 and 6 are shown the curves for the three variable conditions: namely, (1) time allowed for the lake to form, (2) the temperature at which the lake was formed and (3)

TABLE I

VARIATIONS IN QUANTITIES OF REAGENTS

Hydrochloric Acid		Ammonium Hydroxide	
Reagent, cc.	Intensity, %	Reagent, cc.	Intensity, %
0	102	1.5	52
3	105	2.0	100
5	100	2.5	130
8	97		

the volume of the solution when the lake was formed. For (1) and (2) measurements were made at the end of twenty-five minutes and sixty minutes, respectively.

Presence **of Other** Ions.—The intensity of solutions containing 15 mg. of chloride, nitrite, normal phosphate, orthophosphate, sulfate or sulfite ions or of silica was sensibly the same as that of the standard containing only aluminum. Furthermore, the presence of these ions caused no appreciable decrease in intensity at the end of one hour. The final color was not altered by 45 mg. of the orthophosphate ion.

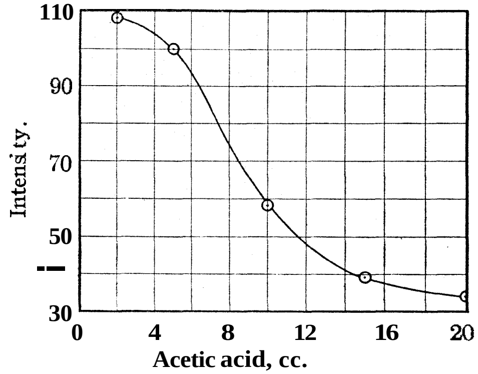


Fig. 4.—Concentration of acetic acid.

With 5 mg. of nitrate ion the intensity was 99% and had not decreased at the end of one hour; with 15 mg. the intensity was 96%, and with 30 mg. it was 39%. With 1 mg. of sulfur as sulfide the intensity was 100%, decreasing to 97% at the end of one hour. Greater quantities yielded a turbid solution.

Solutions containing 15 mg. of chromium as chromate, zinc, calcium or magnesium gave readings in accord with that of the standard. The effects of some other positive ions are summarized in Table II.

An effort was made to prevent iron from interfering by adding ammonium citrate before the ammonium hydroxide, Some representative results are given n the following table:

Citrate, cc.	0	10	10	20	20	20
Aluminum, mg.	0.1	0.0	0.1	0.1	0.1	0.1
Iron, mg.	.0	.0	.0	.0	1.0	5.0
Intensity, %	100	128	131	320	314	388

Limits of the Test for **Colorimetric** Work.—The data for the sensitivity curve, Fig. 7, are shown in Table III.

At the left is shown the volume of solution in liters containing one gram atomic weight of aluminum; *B* is mg. of aluminum in 50 cc. of the

TABLE II

PRESENCE OF OTHER IONS

Ion[a]	Intensity, %, 15 mg.		Intensity, % 10 mg.	Intensity, % 5 mg.	Intensity, % I mg.
Fe^{+++}	heavy ppt.	...	brown ppt.	brown ppt.	100 (0.01 mg.)
Co^{++}	....	177[b]	deeply col.	204	185
Ni^{++}	120	161[b]	103	100	100
Mn^{++}	69	130[b]	69	70	88
Cr^{+++}	deeply col.	...	....	deeply col.	150
Cu^{++}	deep red	...	deep red	200	110
Sn^{++++}	very turbid	...	very turbid	107 (turb.)	103

[a] A 0.1% solution of alizarin used unless otherwise indicated.

[b] A 0.2% solution of alizarin used.

TABLE III

SENSITIVENESS

Volume, liters	B	A	S	B'	B/B'	Δ/B'	$\sqrt{V}/4$	$\sqrt{S}/4$
2,710	0.500	too intense for comparison						
6,775	.200	0.027	37.04	0.227	0.880	0.119	20.6	1.52
13,550	.100	.012	83.33	.112	.893	.107	29.0	2.28
135,500	.010	.0011	909.1	.0111	.900	.099	91.3	7.54
271,000	.005	.0010	1000	.006	.834	.167	130	7.90
1,355,000	.001	.0005	2000	.0015	.733	.500	291	11.12
3,387,500	.0004	barely distinguishable from "blank"						
With 10 cc. of glycerine								
13,550	.100	.015	66.7	.115	.870	.150	29.0	2.04
With 0.2% dye								
13,550	.100	.016	62.5	.116	.862	.137	29.0	1.98

solution; A is the increment in mg. of aluminum necessary to produce a perceptible difference in the color intensity of 50 cc. of solution, $S = 1/\Delta$ = Sensitivity, and $B' = B + A$. For convenience in plotting, one-fourth of the square root of the volume and the sensitivity has been taken.

With 1 mg. of aluminum present the lake had coagulated and settled 1 cm. at the end of two hours; with 5 mg. the precipitate began to settle before the addition of acetic acid, was dispersed by the acid and after two hours had settled, leaving a clear yellow liquid.

For purposes of comparison the aluminum content of three solutions, as determined by Alizarin S and by "Aluminon" are given in Table IV.

TABLE IV

DETERMINATION OF ALUMINUM IN SOLUTION

Solution	Al, mg.	Found by Alizarin S.	by "Aluminon"[a]
I	0.10	0.08	0.12
II	.05	.05	.06
III	.03	.03	.03

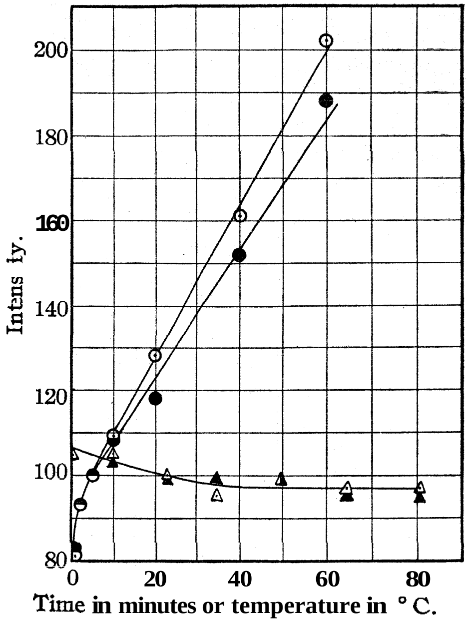
[a] The ammonium salt of aurintricarboxylic acid.

Discussion

The "aging" effects in the light and in the dark are about the same. An increase in the excess of acetic acid increases the rate of change in the color intensity during the first twenty minutes; however, after this time interval all the curves run almost parallel with the axis of time.

Fig. 2 indicates that the intensity is directly proportional to the aluminum content, provided that an excess of the dye is present. With 0.1% of dye the curve breaks at 0.1 mg. of aluminum, and with 0.2% of dye it breaks in the vicinity of 0.2 mg. of aluminum, supporting Atack's opinion[1] that a definite chemical compound is formed, or more likely simply representing an equilibrium condition.

Atack[1] recommends a 1% alizarin solution, but we have found, working with a liquid volume of 50 cc. in Nessler tubes, or in a colorimeter of the Kennicott-Campbell-Hurley type, that it is impossible to use the dye solution stronger than 0.4% on account of the very intense color. Weaker solutions yielded more satisfactory results. Fig. 3 shows a curve for the variation in the amount of dye used.



⊙, Time, "aged" 25 min.; ●, time, "aged" 1 hour; △ temperature, "aged" 25 min.; ▲, temperature, "aged" 1 hour.

Fig. 5.—Conditions at lake formation.

Variations of less than 1 cc. in the quantity of hydrochloric acid produce a negligible effect on the results; however, the final intensity is very sensitive to slight variations in the concentration of ammonium hydroxide. This is probably due to the alteration of the excess acetic acid by the ammonia.

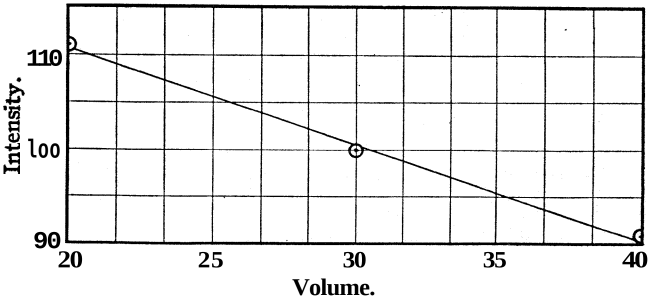


Fig. 6.—Volume at lake formation.

The temperature effect (Fig. 5) is very slight, while the intensity increases quite rapidly with the time given for the lake to form. The volume effect (Fig. 6) is practically the same as in the case of "Aluminon."

One mg. of sulfur as sulfide, or 10 mg. of nitrate ion may be present in 50 cc. of solution without the results being impaired. One mg. of stannic tin is allowable, but the copper content must be considerably less than 1 mg. Ten mg. of nickel is permissible; iron, chromium, cobalt and manganese must be removed if present in more than a trace. The use of a citrate to prevent the interference by iron and chromium was not successful. Fifteen mg. of the other positive ions studied do not interfere with the determination.

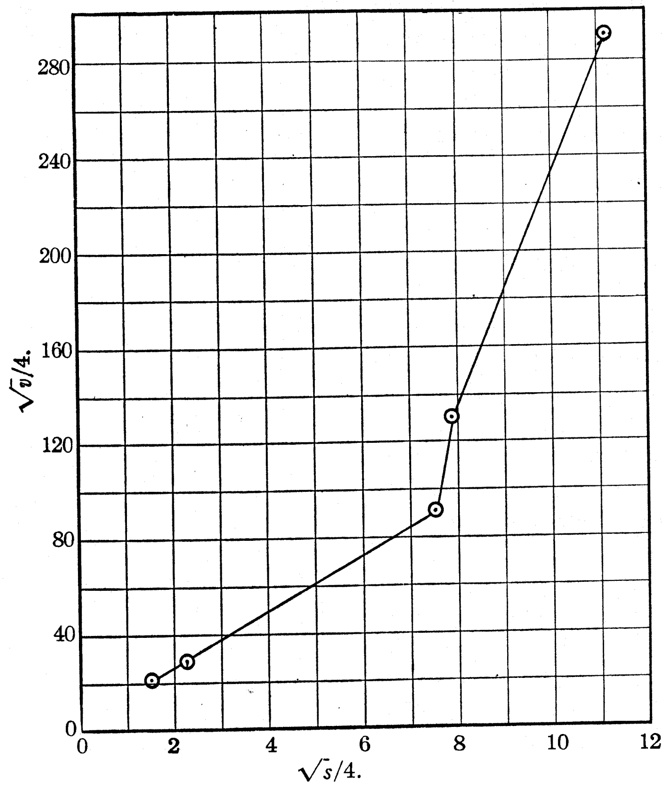


Fig. 7.—Sensitivity curve.

With 50cc. Nessler tubes the range of the test is from 0.0004 to 0.2 mg. of aluminum; with a volume of 50 cc. in the Kennicott-Campbell-Hurley colorimeter 0.005 to 5 mg. may be determined. The lake produced by 10 mg. of aluminum remains in suspension long enough for a reading to be taken, but a smaller volume of the liquid must be employed. By using glycerine greater quantities may be kept in suspension.

According to the method of Horn,[3] the sensitivity curve (Fig. 7) shows that with 50cc. Nessler tubes the best range of the test is from 0.01 to 0.2 mg. When glycerine or a stronger solution of the dye is employed, the sensitiveness is decreased considerably.

Summary

An experimental study of the reaction of Alizarin Red S with aluminum under various conditions has been made, and quantitative measurements on the following effects were obtained: (1) time, (2) temperature, (3) volume, (4) concentration of reagents and (5) the presence of other ions. The range and the sensitiveness of the test have been determined.

UNIVERSITY, VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. I. THE PREPARATION AND STABILITY OF SOLUTIONS OF CERIC SULFATE (CONTAINING FREE SULFURIC ACID). II. POTENTIOMETRIC STUDY OF THE REACTIONS BETWEEN CERIC AND FERROUS OR OXALATE ION. APPLICATION TO THE STANDARDIZATION OF CERIC SOLUTIONS. III. THE POTENTIOMETRIC DETERMINATION OF CERIUM

BY N. HOWELL FURMAN

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Introduction

Barbieri[1] was apparently the first to propose the use of a solution of ceric sulfate in volumetric analysis. He described the direct titration of nitrite with ceric sulfate. The end-point was determined by the disappearance of the yellow color of the ceric ion (the nitrite solution was placed in the buret). He found that more exact results could be obtained by adding an excess of ceric solution. The excess of ceric salt was then determined iodimetrically. It was stated that the nitrite solution could contain nitrates and that the ceric solution need not be free from other rare earths. No experimental data were given.

A solution of ceric sulfate, or of other ceric salts, was found by Sommer and Pincas[2] "to be ideal" for the quantitative oxidation of hydrazoic acid. The volume of nitrogen that was evolved was measured.

Quite recently Martin[3] has used ceric sulfate for the oxidation of hydra-

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[3] Horn, Am. *Chem.* J., 36, 195 (1906).

[1] Barbieri, *Chem.-Ztg.*, 29, 668 (1905).

[2] Sommer and Pincas, Ber., *48*, 1963 (1915).

[3] Martin, THIS JOURNAL, *49*, 2133 (1927).

zine. The reagent was added in excess and an iodimetric back-titration was then made.

Hitherto, perhaps because of a lack of satisfactory indicators, no systematic study of the direct and indirect applications of ceric sulfate in volumetric analysis has been made. The author has found that ceric sulfate solutions that contain a moderate excess of sulfuric acid are quite stable, and he therefore proposes to make such a study. The familiar methods of potentiometric titration will be shown to be especially suitable for the determination of end-points.

Mention should be made of the fact that Van Name and Fenwick[4] have published graphs that represent the potentiometric titration of ceric with titanous sulfate. No data were given with regard to the accuracy, since these titrations were incidental to a study of bimetallic electrode systems. Recently Someya[5] has made a study of the potentiometric adaptation of Metzger's[6] bismuthate procedure for the oxidation of cerium. Someya titrates the quadrivalent cerium directly with standardized ferrous sulfate.

Preliminary qualitative orientation studies make it appear probable that a number of the titrations with ceric solution as reagent will be of both theoretical and practical interest.

Experimental

Preparation of Solutions of Ceric Sulfate in Dilute Sulfuric Acid.—The raw material was in some cases commercial cerous oxalate and in others mixed oxides of the rare earths.[7] In some instances (see Table I for details) no attempt was made to separate the cerium from the other rare earths. In other cases the details of James' method of basic bromate-nitrate separation were carefully followed.[8] The author found that this method was relatively easy to use and that it made possible the preparation of large quantities (30–50 g.) of pure, ignited ceric oxide in a few hours.[9] The purification was not found to be necessary in order to obtain a "stable" ceric solution. A much higher percentage of the oxide is, however, converted into the sulfate if the oxide is pure. The ceric oxide, whether obtained from the impure oxalate, basic bromate-nitrate or commercial mixed oxides, was heated with a large excess of sulfuric acid (sp. gr. 1.84) as directed by Meyer and Aufrecht.[10] Most of the excess of sulfuric acid was removed

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[4] Van Name and Fenwick, THIS JOURNAL, 47, 9, 19 (1925).

[5] Someya, Z. *anorg. allgem. Chem.*, 168, 56 (1927).

[6] Metzger, THIS JOURNAL, 31, 523 (1909).

[7] The oxides were supplied through the courtesy of Dr. H. S. Miner of the Welsbach Co., Gloucester, N. J.

[8] James, THIS JOURNAL, 34, 757 (1912); also James and Pratt, *ibid.*, 33, 1326 (1911).

[9] Commercial specimens of cerous oxalate are far from pure. In two instances 22.25 and 22.8% of CeO_2 were found, respectively, whereas $Ce_2(C_2O_4)_3 \cdot 10H_2O$ contains 47.5%.

[10] Meyer and Aufrecht, *Ber.*, 37 (1), 140 (1904); it is interesting to note that H. Rose, "Handbuch d. analyt. Chemie," Vol. II, 1871, p. 70, states that ceric oxide is soluble in sulfuric acid without the evolution of oxygen. Spencer, J. *Chem. Soc.*, [2] 107, 1265 (1915), carries out the heating at water-bath temperature. Cuttica and Bonamici *Gazz. chim. ital.*, 53, 761 (1923), state that the CeO_2 should be boiled with the acid.

from the practically insoluble ceric sulfate by decantation. The remaining paste of ceric sulfate and sulfuric acid was treated with cold water little by little. There is usually an insoluble residue of unattacked oxide that must be removed by filtration (asbestos). The author confirmed the finding of other investigators[7,10] that the unattacked residue is much greater when the oxide is impure.

The Stability of Ceric Sulfate Solutions (Containing Sulfuric Acid).--Ceric sulfate solutions are reported in the literature to be unstable.[11] No data are given as to the extent of the instability. There is no *a priori* reason to expect that such solutions should be less stable than equivalent solutions of potassium permanganate.

Data regarding the stability of ceric sulfate solutions that have been accumulated, in part incidentally (Solutions I–IV), in the study of various bimetallic electrode systems, are presented in Table I.

TABLE I

THE STABILITY OF CERIC SULFATE SOLUTIONS (WITH FREE SULFURIC ACID PRESENT)

Time, weeks	Normalities of ceric sulfate solutions					
	I	II	III	IV	V	VI
0	0.02000	0.03334	0.04292	0.04828	0.1093	0.07830
1	.02001	....	....	.04822	.1090	.07830
2	....	.03323	....	....	....	.07832
4	.02001	.03321	....	.04821	.1090	.07832
6	.02004	....	.04274	.04813	....	.07833
12	....	.03306	.04268	.04788	.1094	....

Solutions I and II were prepared from impure CeO$_2$ that was obtained by the ignition of commercial oxalate; No. III from impure commercial oxide; nos. IV–VI from nearly pure oxide that was prepared by James' method.

Between 10 and 40 cc. of free sulfuric acid (sp. gr. 1.84) were present per liter of ceric solution. The normalities of the solutions were determined by adding a measured excessive quantity of freshly standardized ferrous sulfate solution and titrating the excess of ferrous salt with permanganate solution (0.05 or $0.1N$) that had been standardized against pure sodium oxalate. The volumetric apparatus that was used had been carefully calibrated. The normalities that are given in the table are averages of two (in a few instances more) concordant determinations. Solutions I–IV were kept in clear glass bottles and were exposed to diffuse but not direct sunlight; their temperature was not as carefully controlled as was the case for solutions V and VI. The two latter solutions were kept in the dark.

From the data already in hand it appears that dilute sulfuric acid solutions of ceric sulfate possess at. least a moderate degree of stability. Further observations regarding the stability of ceric solutions will be included in future communications regarding the applications of such solutions. The method of Meyer and Aufrecht[10] insures the preparation of ceric solutions that are perhaps more nearly free of halogen than those that are prepared by many other methods (oxidation of precipitated ceric hydroxide with halogens, etc.).

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[11] Brauner, *Z. anorg. allgem. Chem.*, *39*, 286 (1904); Bauer and Glaessner, *Z. Elektrochem.*, **9**, 534 (1903); see also handbooks, for example, Abegg, Mellor, etc.

II. Potentiometric Study of the Reaction between Ceric and Ferrous or Oxalate Ion. Application to the Standardization of Ceric Solutions

In the preceding section it has been shown that ceric solutions acidified with sulfuric acid are quite stable. The reaction between such a solution and a standardized ferrous sulfate solution has many obvious applications; it serves as a convenient means of checking the normality of ceric solutions. A thorough study of the reaction was therefore made.

Experimental

The Ceric–Ferrous Reaction.—The majority of the determinations were made with the same apparatus that has been described elsewhere.[12] The indicator electrodes were spirals of bright platinum wire of 6–8 cm. length (No. 28 B. and S. gage). In all titrations that involve ceric ion it is well to exclude chloride, and hence a bridge of approximately N potassium sulfate solution was inserted between the N calomel electrode (N. C. E.) and the titration beaker A simple slide-wire potentiometer was used in that portion of the work which was done at the analytical chemical laboratory of the **Eidgenössche Technische Hochschule** at **Zürich,** Switzerland.

The potentiometric titration of ceric sulfate with freshly standardized ferrous sulfate in dilute sulfuric acid solution gives accurate results. The jump in potential at the end-point is very large, and under the conditions that were employed (50-100 cc. of solution containing 3-5 cc. of sulfuric acid of sp. *gr.* 1.84). 0.05 cc. of 0.05 N ferrous sulfate produces a change of 0.3–0.37 volt, at the end-point. The potential readings are steady except within a short range (2-5 drops, depending on the dilution) about the end-point. It is necessary to wait a few minutes for the reaction to complete itself (14 minutes) after the addition of each drop of reagent. The potentials tend up if the end-point has not been reached. The data in the following table indicate the accuracy of the determination.

TABLE II

TITRATION OF CERIC SOLUTIONS WITH FERROUS SULFATE

A. Ceric solution 0.0200 N

$FeSO_4$, calcd., cc.	13.66	27.36	13.66	19.68	19.88
$FeSO_4$, found, cc.	13.63	27.41	13.70	19.65	19.87
Error, cc.	− 0.03	+ 0.05	+ 0.04	− 0.03	− 0.01

B. Ceric solution 0.0429 N

$FeSO_4$, calcd., cc.	21.33	21.33	21.50	21.50
$FeSO_4$, found, cc.	21.31	21.37	21.62	21.46
Error, cc.	− 0.02	+ 0.04	+ 0.02	− 0.04

C. Ceric solution 0.1093 N

$FeSO_4$, calcd., cc.	22.65	32.46	32.46	24.44	24.44
$FeSO_4$, found, cc.	22.68	32.41	32.41	24.48	24.50
Error, cc.	+ 0.03	− 0.05	− 0.05	+ 0.04	+ 0.06

The ferrous sulfate solutions that were used were all approximately 0.05 *N*. The calculated values are based upon averages of two or more concordant determinations that were made by adding standard ferrous sulfate in excess, followed by back-titration with permanganate; the end-points were determined potentiometrically. The results that are given are representative of a much larger number of observations. The

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[12] Furman, J. *Chem. Education,* 3, 932 (1926).

determination is accurate over a wide range of dilutions. The general nature of the titration graph is indicated by Curve 1, Fig. 1. The disappearance of the ceric color cannot be observed accurately enough to serve as end-point indication in 0.05 *N* solution. The yellow color disappears from 1–3 drops before the potentiometric end-point and serves as a convenient warning of the approach of the end-point. These observations were made before the work of Someya[6] appeared. The observations of the author are in complete accord with Someya's description of the potentiometric titration of ceric with ferrous ion. He did not, however, study the titration of ceric solutions of known content; the results that are here presented extend the range of dilutions over which the reaction is known to be accurate. Someya states that a calomel half cell was used. but makes no mention of the use of a salt bridge.

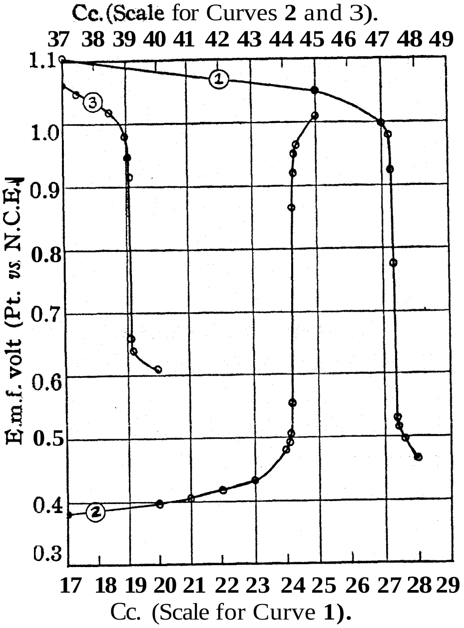

Fig. 1.—Curve 1, titration of 50 cc. of 0.0200 N ceric sulfate with 0.03654 N ferrous sulfate (abscissas at bottom of figure). Curve 2, titration of 50 cc of 0.0691 N ferrous sulfate with 0.0783 N ceric sulfate. Curve 3, titration of 50 cc. of 0.0783 N ceric sulfate with 0.1000 *N* oxalic acid (abscissas for Curves 2 and 3 are above the figure).

The reverse titration, which has not hitherto been described, was found to be accurate. Here again the potentials are not established immediately, in the neighborhood of the equivalence point. The same effect is noticeable in the potentiometric titration of ferrous ion with permanganate under like conditions. If the end-point has not been reached, the potentials tend down. A few representative results follow.

The accuracy is, therefore, of the same order as in the reverse titration. Additional observations were made with more dilute and more concentrated solutions; the accuracy was of the same order as for the data that have been presented. Curve 2, Fig. 1, is a representative titration graph.

TABLE III

TITRATION OF APPROXIMATELY 0.05 N FERROUS SULFATE WITH CERIC SULFATE (0.04822 OR 0.0546 *N*)

Ceric, soln. calc., cc.	25.55	25.55	26.28	26.28	22.59
Ceric, soln. found, cc.	25.57	25.50	26.30	26.25	22.56
Error, cc.	+ 0.02	− 0.05	+ 0.02	− 0.03	− 0.03

It seems obvious that ceric sulfate solutions may be used for the determination of iron or, conversely, may be standardized against ferrous solutions of known strength. Titrations of separate specimens of Mohr's salt, that contained 14.29 and 14.23% of Fe by permanganate analysis (theory, 14.24%), yielded an average normality of 0.07820 for a ceric solution that was found to be 0.07830 N ($FeSO_4$-$KMnO_4$) and 0.07832 *N* iodimetrically.

Other Electrode Systems.—It was found possible to use the Pt-gold amalgam electrode system that the author has described[13] for ceric-ferrous titrations. The titration errors found were −0.01, +0.04 cc. (titration with ferrous) and +0.03, −0.03, +0.00 cc. in the reverse titration. The Pt-W "galvanometric" method that Furman and Wilson have described[14] gave errors of −0.03, −0.01, +0.03 cc. (titration with ferrous), and +0.03, +0.05, and −0.01 cc. (titration with ceric). The resistance was 150,000 ohms and end-point deflections of 10–14 galvanometer divisions were found. The rated sensitivity of the galvanometer was 0.15 micro-ampere (per division) (Leeds and Northrup Co., No. 2310-D).

The Reaction between Ceric and Oxalate Ions. Application to the Standardization of Ceric Solutions.—This reaction seems to afford a convenient method of standardizing ceric solutions. When a ceric solution is titrated with oxalic acid satisfactory results are obtained if the ceric solution is at 50–60°. At room temperature the reaction is very slow near the end-point, as one would expect from the work of Benrath and Ruland,[15] who studied the kinetics of the reaction. At the higher temperature the reaction is rapid and the ceric color is enhanced, probably because of increasing dissociation of the ceric complexes, and the disappearance of the yellow color gives a sharp end-point with good illumination. Observations that were made during the course of potentiometric studies showed that the color end-point is on the average 0.03 cc. before the potentiometric for approximately 0.1 N solutions.

An exactly 0.1 N solution of oxalic acid was prepared by dissolving 6.700 g. of pure sodium oxalate in water that contained 10 cc. of sulfuric acid of sp. gr. 1.84, and diluting to a liter. Such a solution has been shown to be stable when shielded from light, whereas oxalic acid alone is unstable in solution.[16] The ceric solution had been found to be 0.07833 N (av. of four concordant determinations with ferrous sulfate in excess, followed by titration with permanganate that had been standardized against the same sodium oxalate). By direct titration with 0.1 N oxalic acid the ceric solution was found to be 0.07828, 0.07836, 0.07826, 0.07820, 0.07840, average 0.07830. Expressed in terms of cc. of error on the assumption that the permanganate values are correct, the deviations are −0.01, +0.01, +0.03, −0.03, +0.05. The buret delivered 0.025 cc. per drop; either 25 or 50 cc. of ceric solution was titrated. The potential values are imme-

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[13] Furman, This Journal, 50, 268 (1928).

[14] Furman and Wilson, *ibid.*, 50, 277 (1928).

[15] Benrath and Ruland, *Z. anorg. allgem. Chem.*, 114, 267 (1920).

[16] Beckurts, "Massanalyse," Vieweg and Son, Braunschweig, 1913, or Treadwell-Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, for details.

diately steady to within 0.1–0.2 cc. of the end-point. No precipitate of cerous oxalate is farmed until several cc. of oxalic acid have been added beyond the end-point. The character of the titration graph is shown by Curve 3, Fig. 1.

The reverse titration is apparently accurate, but is not practicable because of the slow rate of reaction, even at points remote from the equivalence point. Pure sodium oxalate was dissolved in 50 cc. of solution that contained 5 cc. of concd. sulfuric acid. The solutions were at 50°. The average of two titrations yielded a normality of 0.07820 for the ceric solution. No precipitate of cerous oxalate is formed under these conditions.

III. The Potentiometric Determination of Cerium

The work that is here presented has in part been anticipated by the appearance of an investigation by Someya,[5] who studied the application of potentiometric titration with ferrous sulfate to the determination of cerium that had been oxidized with sodium bismuthate.[17]

The author had commenced a comparative study of the potentiometric determination of cerium with ferrous sulfate, after oxidation to the ceric condition by Metzger's[6] method or von Knorre's persulfate method,[18] with a potentiometric method that is very different in principle, namely, the oxidation of cerous salt in potassium carbonate solution by potassium ferricyanide[19] that has been proposed by Tomiček.

The results that had been obtained at the time of the appearance of Someya's work will be presented briefly because they confirm his experience, and in addition show that the bismuthate, persulfate and ferricyanide methods are in substantial agreement.

In studying the potentiometric application of the ferrous titration to solutions of cerium that had been oxidized by persulfate it was necessary to consider the recent work of Lindeman and Hafstad,[20] who have found that the best range of sulfuric acid concentration for complete oxidation with ammonium persulfate is between 2.7 and 9.5 g. of acid per 100 cc. of solution. For quantities of the cerium metals between 0.05 and 0.75 g., they find an optimum acid concentration of about 3.2 g. per 100 cc. They report that constant values are obtained under these conditions, but that if a large quantity of magnesium sulfate is added (at least 5 g. of magnesium per 1 g. of cerium metals) constant results are again obtained that are appreciably higher than the former ones. They found 43.5% of Ce in a given substance when no magnesium was added, and under like conditions 47.5% of Ce with the presence of magnesium, and in another material 31.46% of Ce without magnesium, and 34.50% after the addition.

The author was unable to confirm these latter findings; the excess of cerium that was found was never as large as that reported by Linde-

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[17] Metzger's method, ref. 6; see also Metzger and Heidelberger, *ibid.*, **32**, 642 (1910).

[18] Von Knorre, *Z. angew. Chem.*, **1897**, 685, 717.

[19] Method of Browning and Palmer, *Am. J. Sci.*, **26**, 83 (1908); Tomiček, *Rec. trav. chim.*, **44**, 410 (1925).

[20] Lindeman and Hafstad, *Z. anal. Chem.*, **70**, 433 (1927).

man and Hafstad, nor was the excess constant with variable duration of boiling of the solutions in order to decompose the excess of persulfate. The addition of magnesium sulfate appears to be undesirable, because it alters the acid concentration and also seems to prevent the decomposition of the last traces of persulfate. If two solutions are oxidized under like conditions with 5 g. of magnesium present per g. of cerium metals, then boiling for fifteen minutes to decompose the excess of persulfate gives results that check. If the boiling is continued for thirty minutes, the results again check, but at a lower titer than before. Even one hour's boiling does not bring the titer down to the value that is found when no magnesium is added. The titration graphs show an ill-defined inflection that lies high in the oxidizing region within a few drops of the end-point when magnesium is present in excess; this is apparently due to undecomposed persulfate.

The results of a number of comparative determinations are assembled in the following table.

TABLE IV

COMPARISON OF POTENTIOMETRIC METHODS FOR THE DETERMINATION OF CERIUM

	Method employed							
	Titr. with Fe^{++} after persulfate oxidation			Bismuthate oxidation titr. with Fe^{++}			Ferricyanide (Tomiček)	
	usual meth.	mod. method[a]						
Oxalate "A," % CeO_2	22.89	22.81	23.00 23.07	22.90	22.85 22.90	22.85	22.76	22.70
Cc. of 0.1*N* soln. per 1.3666 g. of oxalate	18.16	18.10	18 25 18.30	18 18	18 13 18.18	18 13	18 07	18.02
Oxalate "B," % CeO_2		22 37	22.55 22.49 22.30 22.37	22 21	22 28			
Ce. of 0.1*N* soln. per 1.4279 g. of oxalate	1 8 . 19.00	19.07	19.22 19.18 19.00 19.07	18.93	18.99			
Ceric oxide (partially purified), % CeO_2	93.50	93.50	94.44 94.92 93.91 94.06	93.52	93.85		93.52	93.84
Cc. of 0.1*N* soln. per 0.3319 g. of oxide	18 03	18 03	18.20 18.29 18.10 18.13	18.04	18.09		18.04	18.08

[a] Method of Lindeman and Hafstad that involves addition of at least 5 g. of magnesium as sulfate per g. of Ce metals before the oxidation.

The customary persulfate, the bismuthate and the ferricyanide methods are in fair agreement. Tomiček's method is convenient when the apparatus has been assembled. The necessity of rigid exclusion of air and of employing large quantities of potassium carbonate militate against the method, In point of time required, the bismuthate and persulfate methods are approximately equivalent, provided the excess of bismuthate must be filtered off. According to Someya[5] this filtration is not necessary if the bismuthate is pure.

The data show that the modification that was suggested by Lindeman and Hafstad[20] does not give results that are mutually consistent or that check with other methods. The determinations that are bracketed together were made at the same time and under as nearly as possible the same conditions. The time of boiling was not accurately recorded for the first sample of oxalate. In the other two instances the first **pair** of determinations was made after 25–30 minutes of boiling, and the second pair after 50–60 minutes of boiling. In all cases where the customary conditions are used, from 20 to 30 minutes' boiling after the end of the oxidation is sufficient to destroy the excess of persulfate, provided the conditions that von Knorre[18] first established are carefully followed.

The determinations that are given for the per cent. of CeO_2 in the oxalates were in part made upon small separate samples, and in part upon solutions of large quantities of the oxalate. In case of the ceric oxide all of the determinations were made upon a uniform solution that was prepared by transposing the oxide to the sulfate. After dilution, reduction was effected by excess of hydrochloric acid, which **was** removed by heating. **A** small quantity of ceric salt escaped reduction and was decolorized with a slight excess of hydrogen peroxide in strongly acid solution followed by boiling to destroy the excess. For convenience in comparison the quantity of exactly 0.1 N reagent per constant weight of substance is given in each case.

Work is now in progress upon direct applications of ceric sulfate in the potentiometric titration of various reducing substances.

Acknowledgment

A portion of the experimental work that is here presented was done in the analytical chemical laboratory of the Eidgenössche Technische Kochschule, Zürich, Switzerland. The author wishes to make grateful acknowledgment of the privilege of working as guest in this Laboratory, and to thank the authorities of the Technische Hochschule, and especially Professor W. D. Treadwell, for making this arrangement possible.

Summary

Solutions of ceric sulfate in diluted sulfuric acid are sufficiently stable to be used in volumetric analysis. It is advisable to use pure ceric oxide in their preparation and to shield the solutions from direct sunlight.

The reaction between ceric and ferrous solutions is suitable for the potentiometric determination of either ion with a high order of accuracy. The reaction is sluggish near the equivalence point but this fact does not cause serious inconvenience. The reaction may be applied in the standardization of ceric solutions and in the potentiometric determination of cerium.

Ceric solutions may be standardized or determined by titration with standard oxalic acid. The ceric solution must be heated. The reverse titration is impractical because of the slow rate of reaction, even **when** the oxalic acid solution is heated.

A potentiometric study of the determination of cerium has been made. Oxidation by bismuthate or persulfate followed by potentiometric titration with ferrous sulfate is a very rapid and satisfactory mode of procedure.

PRINCETON, NEW JERSEY, and
ZÜRICH, SWITZERLAND

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 163]

THE CRYSTAL STRUCTURES OF BETA BENZENE HEXABROMIDE AND HEXACHLORIDE

BY ROSCOE G. DICKINSON AND CONSTANT BILICKE

RECEIVED JANUARY 3, 1928 PUBLISHED MARCH 7, 1928

Introduction

In a previous investigation[1] β-benzene hexabromide,[2] $C_6H_6Br_6$, and β-benzene hexachloride, $C_6H_6Cl_6$, both crystallizing in the cubic system, were found to possess the space group symmetry T_h^6 with four molecules in the cubic unit of structure. The $C_6H_6X_6$ molecule was found to possess a three-fold rotation axis and **a** center of symmetry. Since **all** atoms of any one element are in equivalent positions, and since all atoms are in the general positions,[3] a completion of the structure determination requires the evaluation of three parameters for each element in each compound. In the case of the bromide, where the great majority of all electrons are in the bromine atoms, at least the predominant features of the intensities of x-ray reflection must be determined by the positions of the halogen atoms. Consequently a determination of **the** bromine

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[1] Hendricks and Bilicke, THIS JOURNAL, 48,3007 (1926).

[2] Since this paper confines itself to the beta isomers, the Greek prefix will be omitted.

[3] The coördinates of the general positions in T_h^6 are:

$$(xyz)(\tfrac{1}{2} + x, 4 - y, \bar{z})\ (\bar{x}, \tfrac{1}{2} + y, 3 - z)(\tfrac{1}{2} - x, \bar{y}, \tfrac{1}{2} + z)$$
$$(zxy)(\bar{z}, \tfrac{1}{2} + x, \tfrac{1}{2} - y)(\tfrac{1}{2} - z, \bar{x}, \tfrac{1}{2} + y)\ (\tfrac{1}{2} + z, \tfrac{1}{2} - x, \bar{y})$$
$$(yzx)(\tfrac{1}{2} - y, \bar{z}, 3 + x)(\tfrac{1}{2} + y, \tfrac{1}{2} - z, \bar{x})(\bar{y}, 3 + z, \tfrac{1}{2} - x)$$
$$(\overline{xyz})(\tfrac{1}{2} - x, \tfrac{1}{2} + y, z)(x, \tfrac{1}{2} - y, \tfrac{1}{2} + z)(\tfrac{1}{2} + x, y, \tfrac{1}{2} - z)$$
$$(\overline{zxy})(z, 3 - x, \tfrac{1}{2} + y)\ (\tfrac{1}{2} + z, x, \tfrac{1}{2} - y)(\tfrac{1}{2} - z, \tfrac{1}{2} + x, y)$$
$$(\overline{yzx})(\tfrac{1}{2} + y, z, \tfrac{1}{2} - x)(\tfrac{1}{2} - y, \tfrac{1}{2} + z, x)\ (y, 4 - z, \tfrac{1}{2} + x).$$

parameters seemed to offer an approach to these structures for it could be undertaken with the expectation of avoiding the complicating necessity of simultaneous consideration of more than three parameters.

Experimental Data

For the present purpose it was found desirable to obtain certain x-ray data not previously published. The crystals used were prepared as by Hendricks and Bilicke; from them were made spectral, Laue and powder photographs in the usual manner. Spectral photographs were obtained from (100) and (111) of $C_6H_6Br_6$; that from (111) was especially good and permitted a perhaps better determination of d_{100} than the previous powder data. This new value for the bromide is d_{100} = 10.49 Å., giving a calculated density 3.191 g./cc., while the density observed by Hendricks and Bilicke is 3.197 g./cc. The relative intensities of the spectral reflections are shown in Table I. New Laue photographic data for both compounds, obtained with the primary beam nearly perpendicular to (111) are given in Table II. The axes were so chosen (with respect to a permu-

TABLE I

INTENSITIES OF REFLECTION FROM $C_6H_6Br_6$

Order, *n*	1	2	3	4	5	6
Obs. rel. intensities for(100)	absent	weak	absent	medium	absent	strong
S_{Br} for (100)	0	2.1	0	5.9	0	15.7
Obs. rel. intensities for (111)	absent	very weak	absent	medium strong	strong	absent
S_{Br} for (111)	3.0	2.0	0.2	8.7	16.5	5.5

TABLE II

LAUE PHOTOGRAPHIC DATA FROM $C_6H_6Cl_6$ AND FROM $C_6H_6Br_6$

Form (*hkl*)	$\frac{d_{hkl}}{d_{100}}$	Estimated intensities						S_{Br}	S_{Cl+C}
		$C_6H_6Br_6$			$C_6H_6Cl_6$				
		A0.35 8.	A0.40 A.	A0.45 A.	X0.35 A.	X0.40 A.	A0.46 A.		
279	0.086	0.1	0.1	..	0.15	0.15	..	7.32	9.60
972	.086	.05	.05	..	.0	.05	..	3.07	2.49
10.5.1	.089	..	.2	..	.25	.30	.35	12.30	12.48
5.10.1	.089	.0	.0	..	.0	.0	..	0.51	1.21
916	.092		.05	..	.0	.0	.0	4.34	4.06
196	.092		.0	.0	.0	..	.0	0.76	1.83
10.3.3	.092		.05	..	.0	.05	.1	4.94	5.6
477	.094		.1	.1	.05	.05	.1	5.88	7.18
576	.095		.05	.05	.0	.0	.0	3.45	2.81
756	.095	..	.0	.0	.0	.0	.0	1.1	2.1
294	.099	.0	.0	..	.08	.15	..	1.87	2.51
924	.099	.0	.0	..	.0	.0	..	1.60	1.91
168	.099		.0	..	..	.0	..	1.23	2.52
186	.099		.0	..	..	.0	..	1.63	1.17
367	.103		..	.4	.45	.6	..	11.84	12.33
763	.103			.0	.0	.0	..	2.32	2.23

TABLE II (Concluded)

Form (*hkl*)	$\frac{d_{hkl}}{d_{100}}$	Estimated intensities						S_{Br}	S_{Cl+C}
		$C_6H_6Br_6$			$C_6H_6Cl_6$				
		λ 0.35 Å.	λ 0.40 Å.	λ 0.45 Å.	λ 0.35 Å.	λ 0.40 Å.	λ 0.45 Å.		
267	.106	.0	.0	..	..	.0	.0	2.03	1.86
276	.106	.0	.0	.0	..	.0	.0	1.90	1.15
338	.110	.0	..	..	.0	..	..	0.23	1.34
832	.114	..	.05	..	.0	..	.25	2.18	3.88
823	.114	..	.0	..	.0	.0	.05	0.29	3.14
465	.114	..	..	.2	.4	.45	.5	5.19	6.27
564	.114	..	..	.1	..	.08	.17	3.95	3.90
751	.115	..	..	.2	..	.1	..	7.19	4.14
157	.115	..	..	.05	.0	.0	.0	2.05	1.02
147	.123	.1	.15	..	.1	.15	..	3.51	5.00
417	.123	.3	.4	..	.45	.6	.7	6.28	8.56
156	.127	.0	.0	..	..	.0	.0	1.51	2.03
165	.127	.0	.0	..	..	..	.08	1.80	1.74
723	.127	.05	.1	..	..	.15	.2	3.12	2.91
732	.127	.4	..	.4	.7	..	.9	6.22	9.20
155	.140	.8	..	..	.7	..	..	8.47	11.54
354	.141	..	.15	..	.1	..	.25	2.58	1.87
453	.141	..	.2	..	.25	..	.35	3.53	3.23
362	.143	.8	..	..	.6	..	..	10.82	8.74
263	.143	.0	..	..	.0	..	..	0.98	0.11
136	.147	..	..	.7	..	.7	..	8.42	9.02
163	.147	..	..	.05	..	.0	..	2.23	2.12
153	.169	.55	.7	..	..	..	.7	6.77	5.75
513	.169	.0	.0	..	.0	.0	.0	0.30	0.4
144	.174	1.0	1.2	..	..	1.0	1.0	7.28	6.78
423	.186	.15	.2	..	..	.15	..	1.81	2.10
432	.186	.9	1.0	..	..	1.1	..	5.33	6.42

tation of *h* and *k)* that planes (*hk*0) with k odd appeared in the first order, since the space group had already been shown to be T_h^6, requiring the absence of (*hk*0) with *h* odd. In Table **III** is given a remeasurement of

TABLE III

POWDER PHOTOGRAPHIC DATA FROM BENZENE HEXABROMIDE

Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity	Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity
221	3.49	3.498	10.0	423,432,250	1.955	1.950	1.5
230	2.905	2.912	11.0	441, 522	1.83	1.827	0.5
321, 312	2.805	2.806	3.0	442,600	1.748	1.749	2.0
411	2.47	2.473	6.0	611, 523,532	1.707	1.703	4.0
402,420	2.35	2.348	1.5	612, 621 443, 450	1.64	1.64	2.0
421, 412	2 28	2.29	4.0				

the previous powder photograph[4] with a General Electric Company ruler.[5] The measurements were obtained by setting the line due to *(221)* at *3.49* = $10.49/\sqrt{9}$ Å. Some changes in the assignment of indices to the more com-

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[4] Ref. 1, Table I, p. 3008.

[5] Davey, *Gen. Elec. Rev.*, 29, 128 (1926).

plicated lines will be noticed. In Table IV are given powder photographic data for $C_6H_6Cl_6$. **All** powder data were obtained with Mo $K\alpha$ radiation.

TABLE IV

POWDER PHOTOGRAPHIC DATA FROM BENZENE HEXACHLORIDE

Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity	Form	d_{hkl} Å., obs.	d_{hkl} Å., calcd.	Obs. intensity
200	5.00	5.04	0.5	421, 412	2.20	2.20	4.0
210	4.50	4.57	1.5	422	2.056	2.056	0.3
211	4.11	4.11	7 0	430	2 0 0	2.015	0.3
220	3.56	3.563	0 8	431, 413	1.98	1.975	0.3
221	3.35	3.36	10.0	333, 511	1.932	1 94	1.0
311	3 0 4	3 0 4	2 0	432,423,250	1.87	1.87	1.5
230	2.79	2.79	7 0	512, 521	1.838	1 84	0.8
321, 312	2.70	2.69	6.0	441, 522	1.76	1.754	1.2
400	2.53	2.52	2 0	442, 600	1.67	1.68	1.5
322,410	2.44	2.44	1.0	611, 532, 523	1.635	1 635	4.0
411	2.38	2.375	6.0	621, 612 504, 443	1.58	1.574	1.3
420,402	2.25	2.25	2.0	541, 514	1.56	1.555	1.0

The Bromine Parameters

A systematic determination of the bromine parameters did not seem practicable; consequently values were sought by trial. Since the usefulness of a result obtained in this way depends solely on its adequacy to account for experimental material, we shall confine ourselves largely to a discussion of the results finally obtained. It may be said, however, that the trials were made without reference to consideration of interatomic distance. The general course pursued was to neglect the effect of the carbon and hydrogen atoms and to find a set of parameter values which would make the structure factor S for the sixth order for (100) greater than that for the fourth, and that for the fourth greater than that for the second. Many sets of values satisfying these conditions were, of course, found which did not then satisfy the conditions imposed by the (111) reflections, namely, that the fifth order should be greater than the fourth and both of these much greater than the first, second and third. Use was also made of the observation from a (100) spectral photograph that (411) is stronger than (311) and (211) all in the first order. Further elimination and refinement of the parameter values was then made with the Laue data. It is interesting that when the values had been sufficiently refined to account for a small portion of the Laue data, considerably more data were then accounted for without the necessity of further change. The values finally obtained[6] are $x = 0.39$; $y = 0.22$; $z = 0.085$.

In Table I are included values of the structure factor S_{Br} for the bromine atoms alone computed with the above parameters. Except in the case of

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[6] An equivalent set of parameters is $x = -0.11$, $y = 0.28$, $z = -0.085$, which gives directly the coordinates of an atom nearest the origin.

the first order from (111), the agreement with the observations is good; neglect of the carbon atoms is most likely to cause error in such cases of weak reflections with large values of d/n.

In the Laue data of Table II are included only reflections from planes with interplanar distances down to 0.90 Å.; below this the assignment of indices became somewhat uncertain. Intensities have been estimated at three different wave lengths by short interpolations, when necessary, on plots of intensity against wave length. Whenever, at a given wave length, a plane reflects more strongly than one with a larger interplanar distance, it is found to have the larger structure factor. This agreement affords an extensive test of the parameter values.

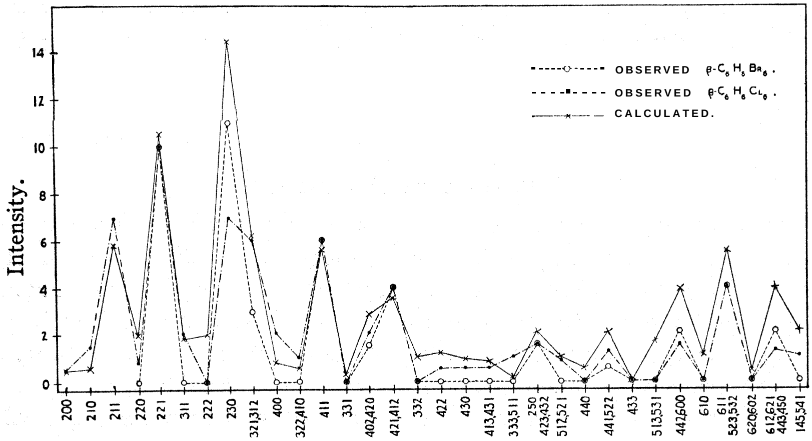

Fig. 1.—Observed powder photographic intensities from $C_6H_6Cl_6$ and $C_6H_6Br_6$ and intensities calculated for the halogen alone.

Comparison of the Laue data for benzene hexachloride with that for benzene hexabromide shows for the most part a parallelism in the intensities even for complicated reflections. From this it seems that the halogen parameters cannot be more than slightly different in the two compounds.

In Fig. 1 is given a graphical representation of the observed powder photographic intensities together with a set of calculated intensities whose relative values were obtained from the empirical[7] formula $I \propto S^2(d/n)^{2.35}$, using for the structure factors S the values obtained for the halogen alone, placing as before, $x = 0.39$, $y = 0.22$ and $z = 0.085$. Since the powder data include many reflections not employed in obtaining the parameters, the general correspondence between the observed and calculated values gives considerable confirmation of the approximate correctness of the parameter values.

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[7] Wyckoff, "The Structure of Crystals," Chemical Catalog Company, New York, 1924, pp. 99-107, 199-201.

Discussion of the Structure

The parameter values given are such that each bromine atom is surrounded by eight others; two of these are at a distance of 3.40 Å., while the other six are at distances of 2.74 to 3.97 Å. These latter distances, at least, appear reasonable when compared with 4.21 Å., the distance[8] between iodine atoms in stannic iodide and in cadmium iodide. Again, the distance between bromine atoms in lithium bromide is 3.88 Å.

Since there are four $C_6H_6X_6$ molecules in the unit of structure, their centers must be at points equivalent to (0,0,0) or at points equivalent to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The arrangement of the six bromine atoms nearest to (0,0,0) is shown in Fig. 2a. That of the six nearest to $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is shown in Fig. 2b; the latter form approximately a regular octahedron. But more information than the parameter values of the halogen atoms alone is needed to enable us to decide which of these two configurations represents the six bromine atoms belonging to a single molecule. Stereochemical considerations decidedly favor considering the group shown in Fig. 2a as belonging to a single molecule. If a cyclohexane ring be constructed of carbon atoms 1.54 Å. apart (the distance between carbon atoms in diamond) and with the lines connecting the center of one atom to the centers of the adjacent two making the angle 109° 28' (the tetrahedral angle), we may inquire whether it is possible to orient such a ring in either of the bromine configurations in such a way that a bromine atom will lie in a third tetrahedral direction from each carbon atom. With the configuration of Fig. 2b this cannot be accomplished even approximately; but if the cyclohexane ring be placed with its center at (0,0,0) in the manner shown in Fig. 2c, the bromine atoms fall very closely in tetrahedral directions from the carbon atoms. Moreover, their distance from the carbon atoms, 1.94 Å., appears to be a reasonable one.[9]

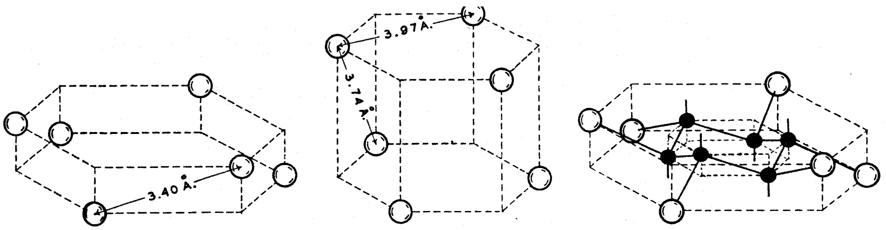

Fig. 2a. Fig. 2b. Fig. 2c.

Fig. 2.—(a) Arrangement of bromine atoms about (000); (b) arrangement of bromine atoms about $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$; (c) suggested arrangement of carbon and bromine atoms in the $C_6H_6Br_6$ molecule.

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[8] The various interatomic distances used here have been computed from data from the International Critical Tables, Vol. I, 340 ff.

[9] Some idea of what should be a reasonable C-Br distance may be obtained from the

A consequence of the conclusion that a molecule center is at (0,0,0) is that the shortest Br to Br distance, 3.40 Å., occurs within a single molecule, while the other distances of from 3.74 to 3.97 Å. are between bromine atoms of separate molecules.

The calculated carbon parameters corresponding to this arrangement are $x = -0.076$, $y = +0.099$, and $z = -0.065$ for the bromide, and $x = -0.079$, $y = \$0.103$, and $z = -0.068$ for the chloride. In the last column of Table II are given structure factors for the chloride calculated using these parameters for carbon, placing the reflecting power of carbon one-fourth of that for chlorine and using the same parameters for chlorine as found for bromine. The effect of introducing the carbon atoms is in most cases small, but a few cases may be seen where it is important; the agreement with the observations is, on the whole, somewhat improved. The x-ray data appear, then, to be compatible with a molecular model involving the usual cyclohexane ring.

The investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

Summary

New x-ray data from spectral and Laue photographs of benzene hexabromide and from Laue and powder photographs of benzene hexachloride are presented. It is shown that by assigning to the bromine atoms the parameter values $x = 0.39$, $y = 0.22$, and $z = 0.085$ in the general positions of T_h^6, the data for benzene hexabromide are qualitatively accounted for in a satisfactory manner. The intensity data for the chloride are very similar to, but not always identical with, those for the bromide. It is pointed out that these parameter values lead to reasonable interatomic distances and are in agreement with a molecule containing a cyclohexane ring of "tetrahedral" carbon atoms.

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following computation. In SnI_4 the distance Sn to I is 2.63 Å. The difference between the radii of tin and carbon may be taken from the structures of gray tin and diamond. In the former the distance Sn to Sn is 2.80 Å.; in the latter the distance C to C is 1.54 Å. whence we obtain $r_{Sn} - r_C = \frac{1}{2}(2.80 - 1.54) = 0.63$. The difference between the radii of iodine and bromine may be taken from the structures of the cuprous halides in which the copper is surrounded tetrahedrally by halogens. The distance Cu to I is 2.63 Å. and the distance Cu to Br is 2.49 Å.; whence $r_I - r_{Br} = 2.63 - 2.49 = 0.14$, and finally the estimate of the distance C to Br becomes $2.63 - 0.63 - 0.14 = 1.86$ Å.

[COMMUNICATION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

STUDIES IN PHOTOSENSITIZATION. II. A SOURCE OF CADMIUM RESONANCE RADIATION

BY JOHN R. BATES AND HUGH S. TAYLOR

RECEIVED JANUARY 5, 1928 PUBLISHED MARCH 7, 1928

With the broadening of the phenomenon of mercury photosensitized processes to a larger number of reactions[1] it becomes of interest to attempt to extend the field to include other metallic vapors than mercury. A consideration of chemical properties, vapor pressure and resonance potentials shows that sensitization by means of excited cadmium atoms not only ought to prove practical, but also ought to yield valuable results. The resonance lines of mercury, cadmium and zinc, together with their equivalents in gram calories and volts, and the temperature at which the vapor pressure is equal to 0.012 mm. are given in the following table.

TABLE I

RESONANCE DATA AND VOLATILITY OF ZINC, CADMIUM AND MERCURY

Metal	Line	λ	Cals./mole	Volts	T. °C., v.p. = 0.012 mm.
Hg	$1S-2^3P_1$	2536.7	112,000	4.86	50
	$1S-2^1P$	1849.6	152,000	6.67	
Cd	$1S-2^3P_1$	3262.1	87,000	3.78	240
	$1S-2^1P$	2288.8	124,000	5.39	
Zn	$1S-2^3P_1$	3076.9	92,400	4.01	350
	$1S-2^1P$	2139.3	133,000	5.77	

As can be seen, while only one of the resonance lines of mercury is in a region available for use, cadmium and zinc have both in a very convenient part of the spectrum. Moreover, a study of the effects on reactions of quanta of various energy content should prove of interest. Unfortunately, the low vapor pressure of zinc makes this metal less useful for such purposes.

This paper deals with the effect of cadmium atoms in the 2^3P_1 state (3262.1 Å.) on ammonia and hydrogen-ethylene mixtures.

Experimental

A source of cadmium resonance light was sought which would be fairly intense and steady enough for such work. Cadmium arcs of the type of the ordinary quartz mercury arc cannot be made with the pure metal, which tends to wet glass and quartz and to break it when it expands upon solidification. Bates[2] has found that a small amount of pure gallium prevents this. To avoid the use of this element, which is difficult to obtain in pure condition, we have discovered that a 50% cadmium-tin alloy

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[1] Taylor and Bates, THIS JOURNAL, 49, 2438 (1927).

[2] Bates, *Bur. Stand. Sci. Paper* No. 37, 1920.

serves the purpose. The alloy melts from 176–200° and does not crack the arc upon cooling. The light emitted is almost entirely that of the cadmium spectrum, because of the low vapor pressure of the tin. A photograph of the spectrum, with one of mercury for comparison, is shown in Fig. 1.

The arc in use in this work was of the Cooper Hewitt type, has been run for over 50 hours and allowed to solidify many times without cracking and has proved in every way satisfactory. It runs at from 7–10 amperes and has the non-restricted character of the cooled mercury arc as used by us for earlier photosensitized reactions.

The experimental arrangement was the same as that used in Part I of this work and described as the static system. The reaction vessel, however, was placed in an electric furnace with a window fitted with a filter of G986A Corning, 5 mm. in thickness, to transmit only the line at 3262 Å. and absorb completely 2288 Å. Filings and shavings of cadmium were placed in the reaction tube, which was brought close to the window and the arc placed on the other side as close as could be without causing local overheating and consequent cracking of the filter.

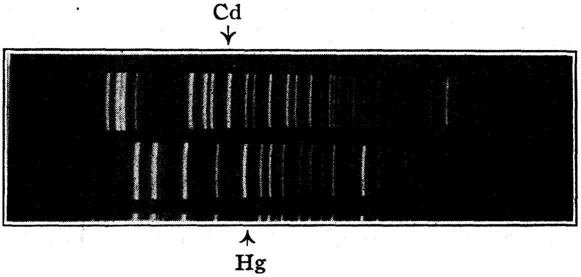

Fig. 1.

Preliminary runs with ammonia and ethylene-hydrogen in the presence of cadmium at 250–260° showed that neither the decomposition of ammonia nor the formation of ethane nor the decomposition of ethylene took place as purely thermal reactions under these conditions. No change of pressure was observed after three to four hours. Before every run the reaction vessel was baked out in *vacuo* above the temperature used for the reactions.

Ammonia, in the presence of cadmium vapor, showed no decomposition after five hours' exposure to the 3262 Å. line at 255–260°.

An ethylene-hydrogen mixture, 545 mm. total pressure and consisting of 273 mm. of ethylene and 272 mm. of hydrogen decreased to 452 mm. after 9 hours' illumination in the presence of cadmium vapor at 255–260°. Forty-seven per cent. of the resulting gas was condensable in liquid air. If the reaction were solely condensation of ethylene, 33% should condense; if the formation of ethane were the sole reaction, 60% should condense. The cooling effect of the liquid air was probably large and so the 47% is probably a high value. For this and other reasons we are led to believe that ethylene condensation is practically the sole reaction.

Theoretical

The probability that two colliding atoms or molecules will have an amount of energy Q available for chemical change, due to their energy of translation, that is, whole component of relative velocity parallel to the line of centers is greater than a value necessary to obtain the energy Q, is equal to $e^{-Q/RT}$.[3] Taking the best value for the heat of dissociation of hydrogen as 101,000 calories, we find the Q necessary for the dissociation of a hydrogen molecule by an excited cadmium atom in the 2^3P_1 state to be equal to 14,000 calories. At 260° the ratio of collisions possessing this energy to the total number would be $N_Q/N = 1/10^6$. The reaction of the formation of ethane from hydrogen and ethylene under the influence of excited cadmium atoms would be one millionth of that reported for excited mercury atoms. This would not be detectable with our apparatus.

Cario and Franck,[4] in studying the cadmium fluorescence spectrum excited by mercury atoms in the 2^3P_1 state, report cases where, at high temperatures, they obtained the 4800' Å. line of cadmium, due to cadmium atoms in the 2^3S_1 state, which is 1.4 volts (32,000 cal.) higher than the 2^3P_1 for mercury. But, at the same time, the 2258 Å. (2^1P) resonance line, which calls for excitation only 0.5 volt higher than that possessed by the excited mercury atoms did *not* appear. This would seem to show that the 1.4 volts are not the result of purely thermal excitation. An explanation may possibly lie in the formation of metastable 2^3P states and subsequent collision.

The vibrational states of the bydrogen molecules do not enter into the thermal excitation at as low temperatures as 500–600° absolute.

In the case of ammonia the heat of an N-H linkage, calculated from the heats of decomposition of nitrogen (263 kg. cal.), hydrogen (101 kg. cal.) and the heat of formation of ammonia from the molecules (22 kg. cal.), is 98 kg. cal. Here the value of N_Q/N would equal $10^{-4.4}$ and the rate of decomposition would be too small to be measured.

The polymerization of ethylene is in entire accord with Part I of this paper, which showed that the initial reaction is probably the formation of acetylene and molecular hydrogen.

Summary

1. A new type of cadmium quartz lamp is described.

2. Ammonia and probably hydrogen are unaffected by the action of cadmium atoms in the 2^3P_1 state at 255°, but ethylene is polymerized.

3. Theoretical considerations of the reactions are in agreement with these results.

PRINCETON, NEW JERSEY

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[3] Foote, Phys. Rev., 30,292 (1927).

[4] Cario and Franck, Z. Physik, 17,202 (1923).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 164]

THE QUANTUM YIELD IN THE PHOTOCHEMICAL DECOMPOSITION OF NITROGEN DIOXIDE

BY ROSCOE G. DICKINSON AND WARREN P. BAXTER

RECEIVED JANUARY 6, 1928 PUBLISHED MARCH 7, 1928

Introduction

In a paper on "Photochemical Equilibrium in Nitrogen Peroxide," Norrish[1] has described experiments in which a pressure increase was observed when NO_2 in a quartz vessel was illuminated by a quartz mercury vapor lamp. Under illumination the pressure increased rapidly at first, then more slowly, and reached a sensibly constant value after about fifteen minutes. When the illumination was cut off, the pressure dropped rapidly at first and then approached its original value comparatively slowly. The pressure increase could not be accounted for by heating alone. Norrish assumed that NO_2 was decomposed photochemically into NO and O_2; constancy of pressure was then attained when the rate of recombination of NO and O_2 became equal to the rate of photodecomposition of NO_2. This assumption received confirmation from the results of experiments carried out at various NO_2 pressures and with NO or O_2 initially present. Both of these gases cut down the pressure increase, and the NO did so more effectively than the 02, as was expected from the fact that the rate[2] of recombination is proportional to $p^2_{NO}p_{O_2}$.

In the present paper are described first some qualitative experiments which test further the correctness of Norrish's view that NO_2 is photochemically decomposed into NO and O_2, and then some measurements on the quantum yield of the reaction with monochromatic light. In contrast with the previous work, the present experiments were carried out under conditions where recombination should be negligible. Since the recombination is a third-order reaction, its rate becomes small at low pressures; for example, at $p_{O_2} = 0.04$ mm. and $p_{NO} = 0.08$ mm., the rate of decrease of p_{O_2} may be calculated from the measurements of Bodenstein and Lindner to be only 2.4 X 10^{-5} mm./hour at 22°. Hence, by keeping the pressures of the reaction products sufficiently small, it might be possible to treat the reaction simply as a photochemical decomposition rather than as a photochemical equilibrium. In order to measure the small amount of reaction product present in the larger amount of NO_2 used to secure sufficient light absorption, the NO_2 was frozen out with liquid air, and the residual gas measured with a quartz fiber gage,[3] the

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[1] Norrish, J. *Chem. Soc.*, **1927**, 761.

[2] Bodenstein and Lindner, *Z. physik. Chem.*, **100**, 87 (1922).

[3] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914); Coolidge, THIS JOURNAL, 45, 1637 (1923).

use of this procedure under similar circumstances having already been found convenient.[4] Measurements of a small amount of product also facilitate the use of relatively weak monochromatic light sources.

This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The Apparatus

A diagram of the experimental arrangements is shown in Fig. 1. The reaction chamber, A, was a Pyrex tube 20 cm. long and 3.2 cm. internal diameter with plane end windows fused on. Always in communication with this was the bifilar quartz fiber gage, B. The side tube, C, could be immersed in liquid air. This much of the apparatus up to the constriction, D, could be surrounded by a furnace for baking out during evacuation. The stopcock, E, led through the liquid air trap, F, to a McLeod gage, mercury vapor pump, etc. The glass enclosed iron rods, G and H, were used respectively for magnetically moving the tube, J, and breaking off its capillary end.

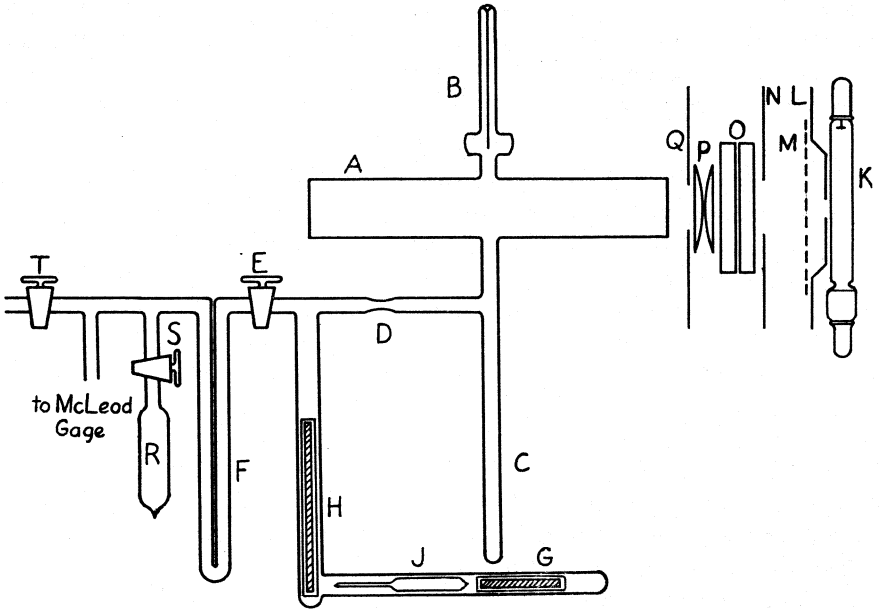

Fig. 1

Light from the mercury arc, K, operated from a storage battery, passed through a hole 1 cm. in diameter in the diaphragm, L. When the shutter, M, was raised, the light passed through the diaphragm, N, the filters, O (described below), and was rendered slightly convergent by the glass

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[4] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, 12, 692 (1926).

lenses, P. The diaphragm, Q, defined the beam entering the reaction chamber; the beam was adjusted to travel the length of the chamber without striking the walls.

The calibration curve for the fiber gage was determined with the aid of the McLeod gage using air, oxygen and at the lower $p\sqrt{M}$ values hydrogen. One fiber gage which we attempted to use showed an unaccountably erratic behavior. Its readings could be markedly altered, for example, by leaning objects against certain parts of the glass apparatus; it seemed as if the vibration period of the gage were in resonance, or nearly so, with some period in the glassware. The gage with which the measurements reported were made was watched carefully and appeared to be free from these difficulties. It had a half-period of 271 seconds at 10^{-3} mm. of O_2, and 18.2 seconds at 4×10^{-2} mm.; nearly all of the measurements were made in this range.

The Materials

The nitrogen dioxide was prepared by heating C. P. lead nitrate in an all-glass apparatus, passing the gas evolved over P_2O_5 and condensing it in a trap cooled by an ice-salt mixture. After condensation of sufficient NO_2, the generating apparatus was sealed off. In preparation for use, the NO_2 was vaporized through a tube containing P_2O_5 and then through a series of small tubes with drawn-out capillary ends; when completely swept out by NO_2 at atmospheric pressure, these were quickly sealed off. The temperature and barometer reading at the time of sealing off were noted and the volumes of the tubes measured later.

The nitric oxide was prepared by the action of mercury on a solution of sodium nitrite in sulfuric acid.[5] The gas was passed over caustic soda, then over P_2O_5 and sealed up in small bulbs.

Tank oxygen was used without other purification than the use of liquid air to remove water vapor.

Tank hydrogen was stored in contact with metallic sodium.

Nitrogen was prepared by heating sodium trinitride.

Preliminary Experiments

The following experiments were made to determine whether a gas noncondensable by liquid air was produced by the illumination of NO_2, as expected, to determine its composition and to ascertain whether its quantity could be used as a measure of the extent of decomposition.

1. The reaction vessel was evacuated and baked out up to the point D. With liquid air applied at C and with the cock, E, closed, a tube, J, containing NO_2 was broken. The cock was opened, traces of uncondensed gas were pumped off and the apparatus was sealed off at D. Enough NO_2 was used to give about 7 mm. pressure at room temperature. The fiber

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[5] Emich, *Monatsh.*, **13**, 73 (1892).

gage was read, the liquid air removed and the apparatus allowed to stand for fifteen minutes in the dark. The liquid air was then replaced and the gage again read. This was done to insure the absence of any unsuspected source of pressure development. The liquid air was again removed and the chamber illuminated for six minutes with the mercury arc without filters, lenses or diaphragms. On replacing the liquid air the pressure was found to be too high to measure and was probably at least 0.15 mm. This experiment showed that a non-condensable gas was indeed produced by illuminating NO_2.

2. Because of the high vapor pressure of liquid NO, gaseous NO alone would not be condensed out by liquid air at the pressures involved here; but in the presence of an excess of NO_2, it might condense out as N_2O_3 or otherwise. To determine whether this occurred, a tube, J, containing enough NO_2 to give a final pressure of 2.8 mm. was introduced and a smaller tube containing NO placed in a second side arm (not shown). The apparatus was prepared and the NO_2 admitted as above, but D was not sealed off. (Separate experiments showed that in these brief experiments the stopcock, E, did not give trouble with NO_2.) With the cock closed the fiber gage was read and the NO then admitted. The gage readings then gave 0.11 mm. of NO. The liquid air was next removed, the NO_2 allowed to vaporize in the dark and the liquid air immediately replaced. The gage showed then as good a vacuum as before the admission of the NO. From the results of such experiments it was concluded that the non-condensable gas produced by the illumination of NO_2 would not contain an appreciable amount of NO.

3. To show that the non-condensable gas was oxygen rather than nitrogen, a side bulb, R, was sealed on and sodium distilled into it in *vacuo* from a second bulb which was then sealed off. Blank experiments showed that oxygen quickly cleaned up when admitted to this bulb through S, whereas nitrogen cleaned up not more than 1%, if at all, in five minutes. The whole apparatus was evacuated and NO_2 transferred from J to C as usual. With stopcock E closed, the liquid air was removed from C and the chamber illuminated for two minutes without filters. The liquid air was replaced on C, and E was opened with S closed. The McLeod gage read 0.14 mm. (total volume of gas about 500 cc.). When the gas was admitted to the small sodium bulb by opening S, the pressure dropped to less than 10^{-4} mm. in three minutes. Experiments also were performed using only the radiation λ 3660 Å., with similar results.

4. These experiments are in agreement with and afford confirmation of Norrish's interpretation of the pressure rise on illumination of NO_2 as being due largely to decomposition of NO_2 into NO and O_2. In order to be able to use the residual oxygen pressure as a measure of the extent of decomposition, it was necessary to be sure that no important amount

of oxygen was removed by the solid N_2O_4 at liquid air temperature. The entire apparatus was evacuated; with liquid air at both F and C, and with E closed, about 0.1 mm. of oxygen was admitted to the McLeod gage system and T closed. Readings of the McLeod gage were made, E was opened and readings were again made. The experiment was then repeated, a considerable quantity of NO_2 having been first condensed in C in the usual manner. Then with E closed, the NO_2 was vaporized from and recondensed in C in the presence of the oxygen; E was opened and the McLeod gage read. The ratio of the initial to the final pressures (about 2.11) was the same to 2% in all cases. Therefore little if any oxygen was removed by the NO_2.

Measurement of Quantum Yield

Previous to each experiment on the quantum yield, the reaction chamber, fiber gage and tube C were evacuated and baked out for several hours without liquid air, and then for a further period with liquid air at F Then liquid air was applied at C, the stopcock, E, was closed, and a tube, J, containing NO_2 was opened; the NO_2 immediately froze out in C. The cock, E, was opened to pump off any residual gas and the apparatus was sealed off at D. The reaction chamber and accessories were then surrounded by a box which was light tight except for provision for admitting the desired radiation. When the NO_2 was subsequently allowed to vaporize for illumination, it came into contact with only glass and quartz. The temperature was not controlled but was always within a degree of 22°.

Three different filter combinations were used to monochromatize the light. Common to all of these was a 1-cm. layer of 6% cupric sulfate solution to remove infra-red.[6] To isolate the blue, λ 4350Å., 4 mm. of Corning glass G585 and 2 mm. of Noviol A were used; for the violet, λ 4050Å., 5 mm. of G586A and 1 cm. of a 4% solution of quinine hydrochloride; for the ultraviolet, λ 3660Å., 9 mm. of G586AW. Mercury arc spectra transmitted by these filters were photographed with various exposure times. The blue radiation contained only the blue Hg lines; the violet radiation contained far less than 1% of the groups at 3650 and 4350; the ultraviolet was free from the lines at 4050 but contained a few per cent. of the wave length 3350.

The intensity of the light entering the reaction chamber was measured in the following manner. At the beginning and end of each illumination the reaction chamber was moved aside and a Moll thermopile with an aperture 6 mm. in diameter was placed in its stead at the center of the diaphragm, Q; the thermopile was connected with a sensitive, low resistance, reflecting galvanometer and a series of measurements of the change

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[6] Coblentz, *Bur. Stand. Bull.*, 9, 110 (1913).

in deflection when the shutter M was opened and closed (by remote control) was made. In these measurements, but not in the calibration, the aperture of the thermopile was covered with a slip of the same glass used for the reaction-chamber window; this automatically corrected for reflection loss. The slight non-linearity of the galvanometer scale was calibrated by measuring the deflections corresponding to small potentials imposed on the galvanometer by a suitable high resistance potentiometer arrangement. The corrected galvanometer deflection produced when the thermopile was placed in a beam of given intensity was determined with the aid of a carbon filament lamp calibrated by the Bureau of Standards; the detailed directions given for the use of this lamp as a radiation standard were followed. The beam entering the reaction chamber was not entirely uniform in intensity over the diaphragm; by taking, in a separate experiment, readings with the thermopile in front of various parts of the diaphragm, a factor was determined to reduce the intensity at the center of the diaphragm to the average intensity over the diaphragm.

Several successive illuminations with corresponding measurements of light intensity and oxygen pressure were made on each sample of NO_2. **As** the half period of a fiber gage is more sensitive to pressure changes the lower the pressure, the first illuminations on a given sample were always briefer than the subsequent ones.

The fraction of the light transmitted by the NO_2 was measured at the end of the experiment by placing the thermopile in a fixed position at the rear of the reaction chamber and observing the change in galvanometer deflection when the shutter was operated both with and without liquid air applied at C. One minus the ratio of these deflections gave the fraction of light absorbed.

At the end of some of these runs (including No. 12, which had the highest final pressure), the apparatus was allowed to stand in the dark for about fifteen hours without liquid air; after replacing the liquid air at the end of this interval, no detectable change in the pressure of the non-condensable gas was observed.

The Experimental Results

In the accompanying table are given the results of all our quantum yield determinations except some with blue light which were found to be unreliable because of stray light and an erratic fiber gage. The partial pressures of NO_2 and N_2O_4 present at the time of illumination were calculated from the volume and temperature of the reaction vessel, the volume of the bulb, J, together with the temperature and barometer reading at the time of sealing it off, and the constant[7] for the equilibrium between NO_2 and N_2O_4. The yield tabulated in the last column is the number

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[7] Schreber, *Z. physik. Chem.*, 24,651 (1897).

TABLE I

QUANTUM YIELD DETERMINATIONS

No.	Wave length, Å.	p_{NO_2}, mm.	$p_{N_2O_4}$, mm.	Fraction of light absorbed	p_{O_2}, initial, mm.	p_{O_2}, final, mm.	Δp_{O_2}, mm.	Exposure time, min.	Galv. deflect., cm.	Yield
5	4350	5.8	0.40	0.902	0.00303	0.00697	0.00394	87.0	8.22	0.0045
					.00697	.01246	.00549	129.0	7.50	.0047
					.01312	.02369	.01057	178.0	8.24	.0059
									Mean	.0050
6	4350	14.2	2.4	.986	.00008	.00691	.00683	147.0	8.90	.0039
					.00691	.01691	.01000	227.0	8.34	.0040
									Mean	.0040
12	4050	3.5	0.15	,753	.00024	.00472	.00448	10.00	3.07	.359
					.00472	.01073	.00601	15.00	2.84	.348
					.01073	.02417	.01344	35.00	2.73	.346
					.02417	.04342	.01925	55.00	2.56	.337
									Mean	.348
11	4050	11.1	1.5	,994	.00055	.00791	.00736	5.00	3.12	.376
					.00791	.01332	.00541	4.00	2.93	.369
					.01332	.02643	.01311	10.00	2.80	.374
									Mean	.373
8	3660	3.5	0.15	.748	.00064	.00558	.00494	5.00	3.42	.792
					.00558	.01112	.00554	6.51	3.08	.757
					.01112	.02393	,01281	15.00	2.91	.804
									Mean	.784
7	3660	9.3	1.0	.982	.00000	.00729	.00729	2.01	4.41	.739
					.00729	.01442	.00713	2.00	4.17	.767
					.01442	.03177	.01735	5.00	3.85	.808
									Mean	.771
10	3660	10.9	1.4	.988	.00093	.00600	.00507	5.00	2.68	.784
					.00600	.01446	.00846	9.00	2.42	.805
					.01446	.02961	.01515	18.00	2.21	.790
									Mean	.793
9	3660	39.7	18.7	.993	.00219	.00711	.00492	5.00	2.78	.729
					.00711	.01343	.00632	7.00	2.61	.714
					.01343	.02504	.01161	13.00	2.48	.742
									Mean	.728

of molecules of oxygen produced per quantum absorbed and was obtained from the following formula,

$$\text{Yield} = \frac{N\cdot r\cdot \Delta p\cdot v}{RT}\left(\frac{d\cdot 10^7 b\cdot A\cdot i\cdot a\cdot 60t\cdot 10^{-8}\lambda}{hc}\right)^{-1}$$

The factor outside the parentheses is the number of molecules of oxygen produced; the factor within is the corresponding number of quanta absorbed. The symbols have the following significance

N = the Avogadro number, 6.062 × 10^{23}
Δp = increase in oxygen pressure, mm. of Hg
v = volume of reaction system, 193 cc.
T = absolute temperature, between 294 and 296" in different experiments
R = gas constant, 82.07 × 760 mm.-cc./degree
r = a correction factor, 1.06, to correct for the fact that 4.5 cc. of the gas was at liquid air temperature

d = mean corrected galvanometer deflection, cm. of scale
b = light intensity to give one centimeter of corrected scale deflection, **11.54** $\times 10^{-8}$ watts/sq. mm.
A = area of diaphragm in square millimeters; **707** in Expts. **5,** 6. **7, 11; 280.5 in** Expts. **8.9. 10. 12**
i = factor to reduce intensity at center of diaphragm to average intensity over diaphragm; 0 84 in Expts. 5, 6, 7, 11; **0.91** in Expts. 8, 9, 10, 12
a = fraction of radiation absorbed
t = time of illumination, minutes
λ = wave length of radiation, Å.
h = Planck's constant, **6.554** $\times 10^{-27}$ erg-secs.
c = velocity of light, **3.00** $\times 10^{10}$ cm./sec.

Discussion of Results

Successive illuminations of a single sample do not show definitely an increase or decrease of yield. This fact affords an additional presumption that the measurements are not seriously in error from such causes as thermal dissociation, recombination or adsorption of oxygen.

In the range of pressures studied, the yields are not markedly dependent on the pressures of NO_2 and N_2O_4. In the determinations with λ 3660Å. the NO_2 pressure was varied 11-fold; the corresponding variation in the N_2O_4 pressure was 125-fold.

The yield is, however, greatly dependent on the wave length of the radiation. The radiation λ 4350Å. is comparatively ineffective, while the radiation λ 3660Å. gives a yield only 23% less than that to which Norrish's mechanism would lead if all the radiation of this wave length produced reaction. The first step in this mechanism is assumed to be the production of a nitrogen dioxide molecule[8] in a higher quantum state, NO_2', by the absorption of a quantum by NO_2. The second step is assumed to be $NO_2' + NO_2 = 2NO + O_2$. In the absence of degradation to heat, or of other loss of the excitation energy, this would lead to the production of one molecule of oxygen per quantum absorbed or a yield of unity.

Two possible explanations suggest themselves for the rapid increase in yield in the neighborhood of λ 4100Å.: (1) Reaction between an excited NO_2 and a normal molecule can take place only when the excitation exceeds a critical energy value, ϵ_0. When the quantum supplied has less energy than ϵ_0, the deficit must be made up from thermal energy; as the deficit will be larger at longer wave lengths, in fewer cases will the thermal energy be sufficient to make it up. However, it is doubtful whether the observed increase in yield with frequency is sufficiently sharp to be accounted for in this manner. (2) The probability that an excited

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[8] Norrish has pointed out that dissociation of NO_2 as a primary process would require the production of an atom of either oxygen or nitrogen; in view of the high energy content of either of these atomic forms, there is not sufficient energy available to permit a dissociation process. That a quantized state is the first result of absorption follows also from the well-known fact that the absorption spectrum is discontinuous. Absorption spectra which we have photographed show this to be true not only in the visible but also in the neighborhood of λ 3660Å.

NO_2 will on collision undergo reaction rather than thermal degradation increases rapidly as its excitation increases in the neighborhood of 70,000 calories per mole (corresponding to violet light).

Summary

Experiments are described which are in confirmation of Norrish's view that gaseous NO_2 is decomposed by light into NO and O_2. By employing a technique permitting experimentation at sufficiently low partial pressures of NO and O_2, recombination of these gases could be made slow enough to neglect. This permitted quantum yield determinations to be made treating the reaction simply as a decomposition rather than as a photochemical equilibrium. For the quantum yields, expressed as molecules of oxygen produced per quantum absorbed, the following mean values were obtained: λ 4350Å., 0.0046; λ 4050Å., 0.36; λ 3660Å., 0.77. These yields were found to be not markedly dependent on the pressure in the range studied.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE COLLEGE]

THE DECOMPOSITION OF POTASSIUM CHLORATE. III. THE EFFECT OF PRESSURE ON THE DECOMPOSITION OF POTASSIUM CHLORATE-MANGANESE DIOXIDE MIXTURES[1]

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The decomposition of potassium chlorate is considered irreversible under any attainable conditions. Lewis and Randall[1a] report that they heated potassium chlorate in a closed steel bomb 1.5 inches in external diameter in which a 0.75 inch hole was bored. After 0.5 hour at 400° the bomb had become bulb shaped. By an indirect method (the comparison of free energies) they calculated that potassium chlorate decomposing at room temperature would be in equilibrium with oxygen under a pressure of about 10^{15} atmospheres and that the equilibrium pressure of the oxygen would rise rapidly with rise in temperature. These results and conclusions are in accord with most of the data on the effect of pressure on the decomposition of potassium chlorate.[2]

Fowler and Grant,[3] however, suggested that the decomposition might be reversible; and Sodeau[4] says of lead chlorate, "It seems remarkable

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[1] A preliminary version of this article was received February 14, 1927.

[1a] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., 1923, pp. 508–511.

[2] (a) Veley, *Phil.* Trans., 179A, 257–295 (1888); (b) Warren, *Chem. News*, 58, 247 (1888).

[3] Fowler and Grant, *J. Chem. Soc.*, 57, 272 (1890).

[4] Sodeau, *J. Chem. Soc.*, 81, 1066 (1902).

that decrease of pressure should markedly impede the decomposition of the chlorate." He used pressures as low as 2 millimeters.

It has been shown[5] that potassium chlorate–manganese dioxide mixtures undergo spontaneous decomposition at quite definite temperatures for definite compositions of the mixture when under atmospheric pressure. As early as 1920 it was known in our Laboratory that mixtures whose spontaneous decomposition temperatures were below 300°, when under atmospheric pressure, could be heated for hours above 325° in sealed steel bombs without complete decomposition of the chlorate.[6] It seemed worth while to make a more thorough investigation of the effect of pressure on the decomposition of potassium chlorate and to include pressures below atmospheric pressure. If high pressures retard this decomposition, even atmospheric pressure might have some retarding effect, and decomposition of potassium chlorate–manganese dioxide mixtures might be produced below 200°.[7]

Apparatus

For pressures below 5 atmospheres the apparatus was made of Pyrex glass. All joints were sealed and no stopcocks were used. When gas was collected at low pressures, the Toepler pump as modified by McLaughlin and Brown[8] was used. Pressures were measured by means of a mercury manometer and a cathetometer.

For work at higher pressures the apparatus consisted of bombs, a connecting block, a pump capable of producing a pressure of 1000 kg. per sq. cm. and connecting tubing and pressure gages such as are used for hydraulic presses. The bombs were made of eighteen-inch sections of steel shafting 2.5 inches in diameter. A three-quarter inch hole was bored to a depth of seventeen inches. The open end was threaded and closed by means of a perforated plug. The outer end of the plug was threaded to fit the hydraulic press connections. The connecting block had four connections and a needle valve so arranged that oxygen could be introduced from a tank, water pumped into the block and connections including the plug of the bomb, and the needle valve closed to cut off the oxygen tank and the pump from the bomb and pressure gage. When no preliminary oxygen pressure was imposed, the pressure gages were connected directly to the bomb. All furnaces were electric resistance furnaces made in our Laboratory to fit the object to be heated. The temperature was regulated by means of a thermo-regulator consisting of a silver rod mounted in an invar steel frame in such a way that the differential elongation was magnified nearly fifty-fold by means of a lever. The contact points on the long arm of the lever completed a circuit which controlled a shunt around the external resistance in the heating circuit.

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[5] (a) Brown, Burrows and McLaughlin, THIS JOURNAL, 45, 1343–1348 (1923); (b) Brown and White, Proc. *Iowa Acad. Sci.*, 31, 291–298 (1924); (c) Burrows with Brown, THIS JOURNAL, 48, 1790 (1926).

[6] Dr. Dwight L. Scoles and Dr. Victor G. Heller did some of the preliminary work on this problem in 1919.

[7] Speaking of potassium chlorate, Mellor says, "The evolution of oxygen begins. . . . with manganese dioxide between 200° and 205°."

Mellor "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. I, Longmans, Green and Co., 1922, p. 350.

[8] McLaughlin with Brown, THIS JOURNAL, 47, 613–615 (1925).

A variation of more than 2° from the mean temperature was unusual even in the experiment which was continued for 300 days. Temperatures were determined by means of mercury thermometers for the lower temperatures, and by means of chromel-alumel thermocouples for the higher temperatures.

Materials

The potassium chlorate used in this work was Baker and Adamson's c. p. grade. A saturated solution gave only a slight cloudiness with silver nitrate. Suitable tests showed the absence of heavy metals, calcium, bromates, nitrates and sulfates. Reduction with excess ferrous sulfate and back titration with potassium permanganate indicated 98.2% of potassium chlorate. Absorbed moisture was the impurity.

The manganese dioxide was prepared by the method of Merrill and Scalione[9] from potassium permanganate and manganese sulfate in strong sulfuric acid. The washing of the precipitated manganese dioxide was continued until it became colloidal and remained in suspension several days after each decantation and addition of distilled water.

The potassium chlorate and manganese dioxide were ground and sifted separately through a 200-mesh sieve, dried at 110°, weighed out and sifted together through a 150-mesh sieve until the mixture was uniform. The composition of the mixture used was $2KClO_3{\cdot}MnO_2$, the composition which Brown, Burrows and McLaughlin[5a] found to have the lowest spontaneous decomposition point.

Experimental Work

The Effect of Low Pressures at Temperatures below 200°.—Equal amounts of the mixture of potassium chlorate and manganese dioxide were carefully dried and placed in each of two hard glass test-tubes with side necks. After sealing the top of each tube, the two were tied together with a copper wire and put into a furnace. The side neck of one of these tubes, in which the material was to be heated at atmospheric pressure, was connected by means of heavy rubber tubing to one end of a glass tube, the other end of which was dipped into a cup of mercury and turned upward to facilitate the collection of gas.

The tube to be heated at reduced pressures was connected to the modified Toepler pump by sealing between them a glass tube containing an enlarged section nearly filled with phosphorus pentoxide.

The results of heating three different samples of the mixture under low pressures are reported in (a), (b) and (c) of Table I. The sample described in part (a) was heated to 100° for two and four-tenths hours and kept under pressures of less than 0.05 cm. for

TABLE I

Low PRESSURE RESULTS

Sample, wt. of $KClO_3$, g.	Temp., °C.	Press., cm. of Hg	Duration of collection, hours	Volume of gas collected, cc.	Cc. of gas evolved per g. per hr.	Vol. of gas calcd. from chloride analysis
(a) 2	125	0.010	6	2.90	0.24	25.1
	145	.010	80	23.00	.15	...
(b) 2	175	.125	3	35.50	5.92	63.9
(c) 1	196–200	.01–.24	3	30.00	10.00	108.0
(d) 2	125	73–75	6	.0	.0	...
	145	73–75	80	.0	.0	...
	175	73–75	3	.0	.0	.0
	196–200	73–75	3	.0	.0	...

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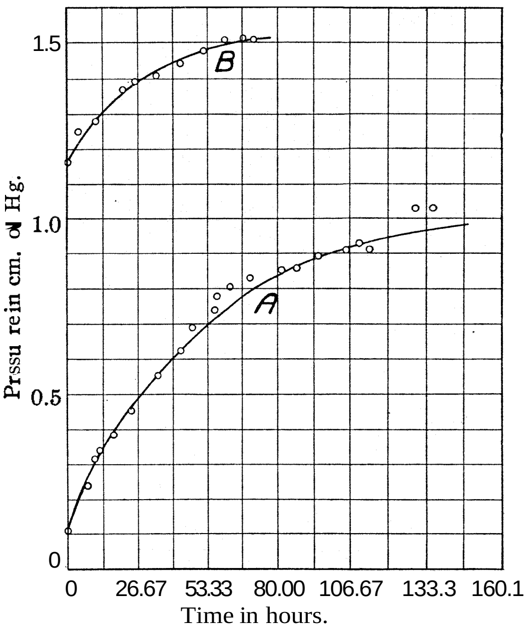
[9] Merrill and Scalione, THIS JOURNAL, 43, 1986 (1924).

more than thirty-four hours beiore any gas was collected. The sample described in part (b) was kept at pressures below 0.07 cm. for eighty-six hours before any gas was collected. On two different days the temperature was raised to 90–100° for one and one-half hour periods. The sample described in (c) was heated to 65–100° for one and one-half hours and kept at pressures below 0.02 cm. for 37.5 hours before any gas was collected. The sample described in (d) was taken from the same supply bottle as the samples referred to in (a), (b) and (c) and was in the furnace with them all of the time but it was subjected to atmospheric pressure during the entire period of the experiments.

At the close of the experiment the apparatus stood for eleven days without any change of reading of the manometer. The gas collected in parts (a) and (b) analyzed 95 and 100% oxygen, respectively. by absorption in alkaline pyrogallate. The gas collected in (c) was lost by an accident. Manganese dioxide absorbs carbon dioxide and the manganese dioxide was exposed to the atmosphere before it was introduced into the test-tube. Carbon dioxide would be absorbed by alkaline pyrogallate. However, the absorption and retention of more than 25–35 cc. of carbon dioxide through 34–86 hours of evacuation, some parts of which were carried out at 100°, on 0.5–1.0 g. of manganese dioxide is unlikely. The formation of chlorides could be due to no cause but the decomposition of some of the chlorate. There is always a close agreement between the amount of oxygen collected and the amount of chloride formed or an excess of chloride formed. The excess of chloride probably corresponds to the amount of oxygen evolved and pumped out before any gas was collected. There seems to be no reasonable doubt that the gas evolved and collected at these temperatures was oxygen.

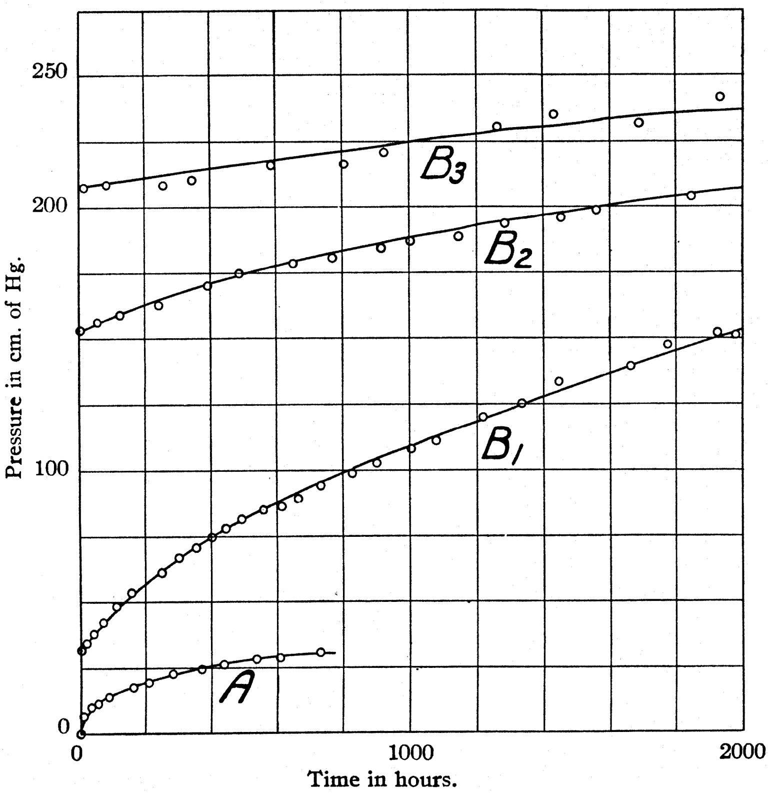


Temperatures 68 and 90°.

Fig. 1.

During the progress of the experiments described in the preceding paragraphs, it was noticed that when the mixture was subjected to pressures less than 0.02 cm. of mercury and heated to 50–60° a small amount of moisture was given off. When the temperature was kept between 60 and 100°, there was evidence that a small amount of gas was being drawn out over the phosphorus pentoxide through the pump—evidently not moisture. In order to determine whether oxygen was given off at these lower temperatures and what pressures would be developed at different temperatures, 10 g. of the mixture, potassium chlorate and manganese dioxide, was sealed in a test-tube and connected to the pump as previously described. The apparatus was evacuated to a pressure of 0.03 cm. The material was heated to 72° and then cooled to room temperature repeatedly for a period of three days. During this time the apparatus was occasionally pumped out, for it proved impossible to keep a constant pressure while the material was being heated and cooled. The pressure did remain constant at 0.05 cm.

for a period of twenty-four hours when the temperature did not average above 50°; but when the temperature was then raised to 60–70° the pressure increased to 0.110 cm. in twelve hours. The temperature was then kept as nearly constant as possible at 68° and the heating continued to determine what pressure would develop. The results are plotted on curve A, Fig. 1. The ordinates are pressures and the abscissas are duration of heating. When the increase in pressure became very slow at 68°, the temperature was raised to 90° without in any way disturbing the apparatus. Curve B, Fig. 1, is a plot of pressure against time for this same charge at 90°. Before the temperature was stabilized, the pressure had risen from 1.03 cm. to 1.16 cm.; so 1.16 cm. is taken as the pressure at zero time for 90°. Curve A on Fig. 2 is a similar plot for a second charge heated at 120°. Curves B_1, B_2, and B_3 on Fig. 2 are a similar representation of data secured at 145° with the same charge which was used at 120°. B_1 represents the first 2000 hours at 145°, B_2 the hours between 2000 and 4000 and B_3 the hours between 4000 and 6000 at 145°.



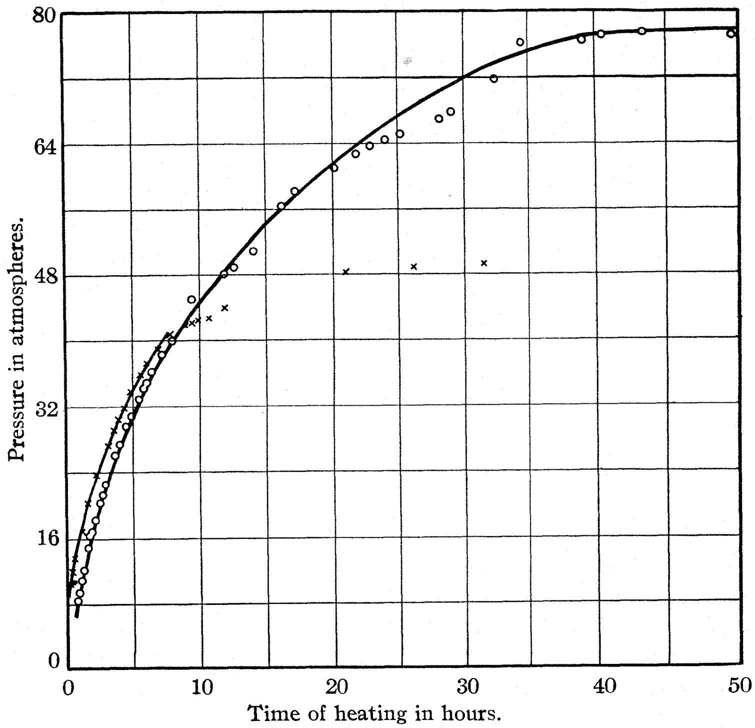
Temperatures 120 and 145°.

Fig. 2.

Two samples were heated at 200° in steel bombs without charging with oxygen. The lowest pressure which the gage recorded was 100 lbs. The curves on Fig. 3 represent the data at 200°. There is close agreement between the curves until a pressure of 40 atmospheres is reached, when the curve marked by crosses indicates a leak.

Many other experiments carried out in the study of the effect of high pressure on the decomposition of potassium chlorate have failed because of explosions or leaks in the apparatus. The following tables contain the results of those experiments in which there was no apparent leak of oxygen.

Before the high-pressure pump and gages were available for measuring the pressure during the progress of an experiment, two apparently successful runs were made. By measuring the volume of the bomb, using the density as found in tables, by weighing each substance in the bomb to determine its volume and by analyzing the residue for chlorides formed by the decomposition of the potassium chlorate, the highest pressure that could be produced by retaining all of the oxygen in the free space



Temperature 200 °.

Fig. 3.

TABLE II

RESULTS AT HIGH PRESSURES—CALCULATED BY THE AMOUNT OF DECOMPOSITION

No.	$KClO_3$. g.	Free space in bomb, *cc.*	Hours heated	Av. temp.. °C.	Press. reached, caled.. atm.	Press. at 20°, calcd.. atm.	Vol of gas at stand. cond., cc.	Cc. of oxygen per g. per hr. (stand. cond.)	$KClO_3$ left in bomb, %
1	28.39	14.6	1.0	335	236.7	99.35	1551.5	54.64	80.2
2	23.57	15.57	7.5	335	322.7	125.63	2230.5	12.62	66.6

of the bomb was calculated. The temperature of the furnace was measured by a mercury thermometer. The results are given in Table II.

The pressures given in Table III were measured on the pressure gage attached to the high pressure pump. The temperatures were measured by a thermocouple. The pressure shown at room temperature at the beginning of each experiment was produced by filling the bomb with oxygen from an oxygen tank through the connecting block as previously described. The charges referred to in Table III were not weighed.

TABLE III

RESULTS AT HIGH PRESSURES—MEASURED BY GAGES

No.	Time heated, hrs.	Average temp., °C.	Pressure, atms.	$KClO_3$ undecomposed, %
1st Expt.	..	Room	200.0	..
	3.0	345	443.3	..
	12.0	Room	280.0	Present[a]
2d Expt.	..	Room	180.0	..
	12.0	Room	180.0	...
	7.0	320	463.3	..
	2.5	290	436.6	..
	3.5	325	480.0	..
	4.0	285	450.0	..
	6.0	320	483.3	..
	5.0	325	496.6	..
	14.0	Room	240.0	*23.5*

[a] Not **quantitatively** determined.

The data under high pressures are not entirely comparable with those under low pressures; for at low pressures the materials were carefully dried while at high pressures the gas was enclosed by a water seal. We have evidence in later experiments that water is very important as a promoter of the catalytic effect of manganese dioxide on potassium chlorate. This promoter effect of water is under investigation in this Laboratory.

Discussion

It is evident that the decomposition of potassium chlorate–manganese dioxide mixtures begins at temperatures far below 200°. Probably there is some decomposition as low as 60°. Certainly at 68° the decomposition progresses continuously if the pressure is kept low enough. The rate of decomposition at a given pressure increases rather rapidly with rise in temperature. At all temperatures below 350" the rate of decomposition is very greatly affected by the pressure of oxygen on the decomposing mixture. This is shown by the experiments reported in Table I. In each of three experiments oxygen was collected from a tube at low pressure while a tube at atmospheric pressure wired to it in the same furnace and charged with the same amount of the same mixture evolved no measurable amounts of gas. Tables II and III show that under pressures of from 200 to 500 atmospheres, potassium chlorate–manganese dioxide mixtures may contain undecomposed potassium chlorate after being held for hours at temperatures as much as 40" above their spontaneous decomposition temperatures at atmospheric pressure. The curves show that the rate of evolution of oxygen decreases faster than the amount of undecomposed chlorate decreases. That this decrease in rate of evolution of oxygen is not due to insufficient contact between catalyst and chlorate is shown by the large increase in rate of evolution when the undisturbed mixture is raised to a higher temperature.

The reaction is not stopped or retarded because of attaining or approaching an equilibrium pressure; for increases of pressure to many times that of the retarding pressure produced no potassium chlorate from oxygen and potassium chloride. Pressures as high as 100 atmospheres of oxygen on potassium chloride–manganese dioxide mixtures at 145° produced no detectable amounts of potassium chlorate in two days. Table III shows that when the temperature is lowered, as from 320°, and brought back to the same temperature again, the pressure is always higher at the return than at the first time that temperature was reached.

Summary

1. Pressure has a marked effect on the rate of decomposition of potassium chlorate in the presence of manganese dioxide within the range of 70 to 350°.

2. For each temperature there is a pressure above which decomposition is very slow or absent.

3. When this pressure has been reached for any temperature, a lowering of the temperature does not result in recombination of oxygen with the potassium chloride and the pressure decreases only as would be expected from the gas laws.

4. Equilibrium for the reaction $2KClO_3 = 2KCl + 3O_2$ has not been attained.

5. The decomposition of potassium chlorate in the presence of manganese dioxide has been effected at temperatures as low as 70".

6. The decomposition of potassium chlorate in the presence of manganese dioxide is retarded by pressures of oxygen below 500 atmospheres when the mixture is heated for periods of several hours at temperatures 40° above its spontaneous decomposition temperature under atmospheric pressure.

7. Water is a promoter in the catalysis of the decomposition of potassium chlorate by manganese dioxide.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LOYOLA UNIVERSITY]

CATALYTIC DEHYDRATION OF ETHANOL BY ALUMINA AT VARIOUS TEMPERATURES

BY A. M. ALVARADO

RECEIVED APRIL 7, 1927 PUBLISHED MARCH 7, 1928

Pease and Yung[1] report that the maximum yield of ether at 275° is 62.00%. Clark, Graham and Winters[2] report yields of ether of over 80.00% at this temperature. It was with the view of determining which of these investigators was right and of throwing further light on the mechanism of the reactions involved in the decomposition of ethanol by alumina that this investigation was undertaken.

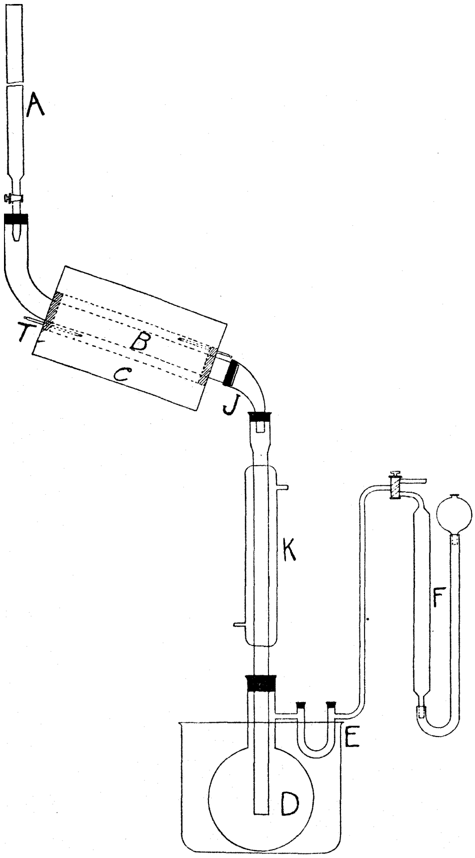


Fig. 1

Materials

Ethyl Alcohol.—The alcohol was prepared according to the method described in a previous paper.[3]

Alumina Catalyst.—The aluminum oxide was prepared by precipitation with ammonium hydroxide from a dilute solution of the nitrate; the solution was boiled to expel the excess of ammonia, the precipitate allowed to settle and the clear supernatant liquid decanted. The precipitate was washed eight times with conductivity water and then filtered through a smooth, hardened filter. The precipitate was dried' for eighteen hours at 240–250°.

Apparatus and Procedure

The apparatus is shown in Fig. 1. A definite volume of alcohol (40 cc.) was allowed to drop at a controlled rate from a buret A into the catalyst

[1] Pease and Yung, THIS JOURNAL, 46, 390, 2397 (1924).

[2] Clark, Graham and Winters, *ibid.*, 47, 2748 (1925).

[3] Pearce and Alvarado, J. *Phys Chem.*, 29, 256 (1925).

Tube B filled with the catalyst, the temperature of which was held constant in an electrically heated furnace C.

The catalyst tube B consisted of a Pyrex tube 2 × 54 cm. and was bent as shown in the figure for convenience of manipulation. The furnace was mounted at an angle of 20° to insure proper drainage of the liquid products. The catalyst tube was connected to the condenser K by means of the adapter J The liquid products were collected in the distilling flask D, completely immersed in a freezing-bath. The gaseous products passed through the side arm of the flask, first into a U tube E, also immersed in a freezing-bath, and then to the gas measuring buret F. The amount of ethylene produced in the reaction was determined by the method of Pease and Yung;[1] the amount of ether by that of Clark, Graham and Winters.[2] The table given by these investigators was used in correcting the observed volumes of ether.

Experimental and Discussion

The results obtained are given in Fig. 2; curves I, II and III represent the ether curves at 269, 300 and 354°, respectively, while IV, V and VI are the corresponding ethylene curves at the same temperatures. An examination of the curves shows that for corresponding times of contact the fraction of ethanol appearing as ether becomes less and less as the temperature increases or, for the same temperature, the fraction appearing as ether becomes less and less as the time of contact is lengthened, the change in the slopes of the curves being more marked at the higher than at the lower temperatures. This seems to indicate that the dehydration of ethanol by alumina is at least a two stage process, the first being the production of ether and the second the dehydration of this ether to ethylene. For a given catalyst the relative proportions of ether and ethylene appear to be dependent upon the temperature and time of contact. The results

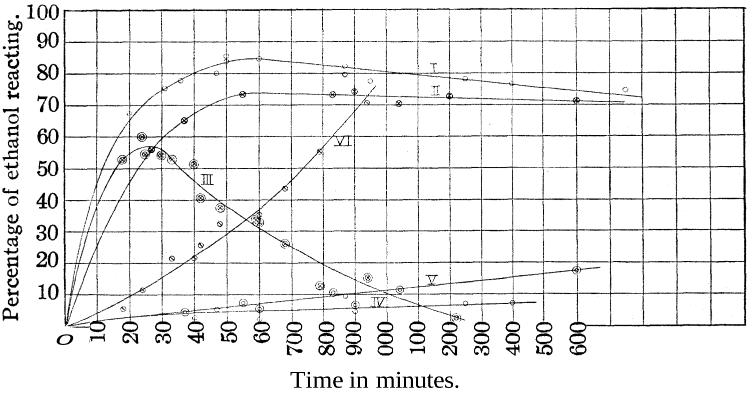


Fig. 2.

here given show that at each temperature the yield of ether passes through a maximum as the time of contact is lengthened. The yield of ethylene, on the other hand, increases continuously. This is in agreement with the results of Pease and Yung[1] at 300°. The maximum yields of ether are, however, higher than those reported by Pease and Yung[1] and are as high as the best yields reported by Clark, Graham and Winters.[2] These maximum yields amount to 82.20% at 269°, 73.50% at 300° and 55.00% at 354°. Pease and Yung[1] report 62.00% at 275°; Clark, Graham and Winters[2] report 85.00% at 275°. The author obtained 82.20% at 269°. The indication is that the higher value is more nearly correct.

Summary

1. The dehydration of ethanol by alumina has been studied at 269, 300 and 354°, respectively, and the results are plotted.
2. Maxima in the ether yields have been obtained at 269, 300 and 354°.
3. The maximum yield of ether at 269 corresponds to 82.20%.
4. A reasonable explanation has been offered for the mechanism of the reactions taking place in the dehydration of ethanol by alumina at the temperatures studied.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES, UNIVERSITY OF THE PUNJAB]

ESTIMATION OF –SOOH (SULFINIC) GROUP AND FE++

BY S. KRISHNA AND HARNAM SINGH

RECEIVED MAY 26, 1927 PUBLISHED MARCH 7, 1928

In a paper on the "Isolation of Sulphinic Acids," Thomas[1] has shown that sulfinic acids give a voluminous precipitate when treated with solutions of ferric salts in strongly acid solutions. These orange colored ferric salts on analysis are found to be of the general formula $(RSOO)_3Fe$, and are insoluble in water and in dilute mineral acids. They are, however, decomposed by alkalies, giving ferric hydroxide and salts of the corresponding sulfinic acids. Sulfinic acids, as a class, have thus been characterized by this property of yielding ferric sulfinates.

It was therefore found desirable to investigate the formation of such ferric salts on quantitative lines, and to employ this method for the estimation of –SOOH group in organic compounds. The importance of this is apparent when it is known that sulfinic acids, which are fairly strong acids, cannot be estimated by titration against standard alkalies when other negative groups (such as, COOH, SO_3H, etc.) are present in the molecule.

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[1] Thomas, *J. Chem. Soc.*, **95**, 342 (1909).

Experiments have shown that the formation of insoluble salts is confined to the sulfinic acid group alone; such other groups as mentioned above are not affected at all, though the compounds containing a carboxyl group give a buff colored precipitate with ferric chloride in neutral solutions, which, however, dissolves in dilute acids.

It has been found in the present work that the formation of ferric sulfinates is quantitative, and this suggested an interesting portion of the problem, the estimation of Fe^{+++} in soluble ferric salts. Another interesting fact which has been noticed is that the sulfinic acids form no such salts with Fe^{++} and this consequently gives us a method of separating Fe^{+++} from a mixture of Fe^{+++} and Fe^{++}. This process can also be employed for the quantitative estimation of Fe^{+++} and Fe^{++}, and thus simplifies the methods hitherto employed for their estimation in the presence of each other.

The formation of sulfinates has been studied with such metals as nickel and cobalt, which occur with iron in the periodic table, and chromium and aluminum, which are closely related to iron in qualitative analysis, and such sulfinates, if formed at all, are unstable under the conditions of the experiments. Therefore the method is applicable where it is desired to estimate or isolate Fe^{+++} in the presence of Ni, Co, Cu, Al, etc.

Experimental

Preparation of Standard Solutions

Ferric Chloride.—Ferric chloride solutions of the following eight concentrations were used in the experimental work: 1, 2, 3, 4, 5, 6, 9 and 15%. These were prepared by dissolving known amounts of ferric chloride in water for different concentrations and the amount of iron per liter was determined by the usual methods of reduction of ferric to ferrous and titration against a standard dichromate solution.

Sulfinic Acid Solutions.—These were prepared by dissolving known weights of sulfinic acid in boiling water. If the sulfinic acid is added to cold water and then warmed, it usually changes to an insoluble disulfoxide and disulfone:

$$RSOOH + HOSOR = RSO_2SOR + H_2O$$
$$RSO_2SOR + O \longrightarrow RSO_2SO_2R$$

Since the solubility of sulfinic acids is not great, only low concentrations were tried. An attempt was made to raise the concentrations by employing alcoholic solutions, but without success because the presence of alcohol interfered in the titrations against standard oxidizing agents. Therefore only about 1% solutions of the sulfinic acids have been used in these experiments.

Reducing Agents Employed.—Two reducing agents (stannous chloride in strong hydrochloric acid or zinc dust and sulfuric acid) have been used side by side for the reduction of ferric to ferrous, and both of these have been equally reliable for these experiments, the former being the more convenient.

Indicators Employed.—Two external indicators were employed in these experiments: a weak solution of potassium ferricyanide in the titration with potassium dichromate of ferrous chloride solution (to determine the complete oxidation of ferrous to ferric) and a dilute solution of potassium sulfocyanide in the titration of sulfinic acid solution and ferric chloride (to see whether or not the Fe^{+++} has been completely used up by sulfinic acid).

Sulfinic Acids.—These were prepared by the usual methods from the corresponding sulfonyl chlorides. As the literature on the subject does not give complete details for obtaining sulfinic acids in good yields, it is thought desirable to give an account of a typical reduction of the sulfonyl chloride to the corresponding sulfinic acid.

A mixture of 20 g. of the sulfonyl chloride, 50 g. of sodium sulfite ($Na_2SO_3 \cdot 9H_2O$) and 100 g. of crushed ice was shaken for three hours until the sulfonyl chloride had dissolved. The mixture was tested for alkalinity from time to time and dilute sodium hydroxide was added to prevent the formation of sulfur dioxide. The mixture was kept cold by further addition of ice, any undue increase of temperature being fatal to the success of the experiment on account of hydrolysis of the sulfonyl chloride. The mixture was filtered and acidified slowly with cold, concentrated hydrochloric acid, when sulfinic acids (usually crystalline) separated. The yield of sulfinic acid is in almost all cases about 80–90%. Recrystallized acids were dried thoroughly by keeping in a vacuum desiccator before using. These gave the usual test with phenetole and sulfinie acid (Smiles Test).

Estimation of $-SOOH$ Group.—A known volume (10 cc.) of ferric chloride solution of a definite concentration was taken and acidified with dilute hydrochloric acid and to it was added a known volume (10 cc.) of the sulfinic acid solution. An orange colored precipitate of ferric sulfinate appeared. This was filtered, washed well with hot water and in the filtrate, which contained excess of ferric chloride, iron was determined by the method already mentioned. Knowing the amounts of iron in the ferric chloride solution before and after treatment with the sulfinic acid solutions, the strength of sulfinic acid was calculated according to the following equation

$$3RSOOH + FeCl_3 = (RSOO)_3Fe + 3HCl$$

In this way the experiments were performed with eight different concentrations of the ferric chloride solution, ranging between 2.01 g. and 28.95 g. of iron per liter. As the trend of error in all the eight experiments was similar, results obtained at extreme concentrations are recorded below.

TABLE I

RESULTS AT EXTREME CONCENTRATIONS

Weight of Sulfinic Acids = 0.1000 g

			Wt of Fe^{+++} = 0 0201 g		Wt. of Fe^{+++} = 0.2895 g.	
Sulfinic acids	**M. p., °C.**	**Method of preparation[a]**	**Wt of acid found, g**	**Error**	**Wt. of acid found, g.**	**Error**
Benzene-	85	1	0.1001	$0.0001	00994	−0.0006
p-Toluene-	86–87	1	.1006	+ 0006	.1007	+ .0007
1,4-Dichlorobenzene-2-	180–182	2	.0999	− 0001	1002	+ 0002
1-Chloro-4-nitrobenzene-2-	139	3	1002	+ 0002	0995	− .0005
m-Benzoic acid	197–198	1	.0995	− .0005	1005	+ .0005
1,4-Dibromobenzene-2-	140		.1007	+ .0007	.1001	+ .0001
p-Chlorobenzene-	93–94	1	.0997	− .0003	0999	− .0001
p-Anisyl-	97–98	1	.0998	− .0002	.0998	− ,0002
p-Acetanilide-	160	2	.0999	− 0001	.1008	+ .0008
Salicylic acid-4-	159	2	.0999	− ,0001	0999	− .0001
m-Benzene-disulfinic	118–119	4	.0996	− 0004	.0994	− .0006
Cinnamic acid *p*-sulfinic	140–142	2	,1027	+ .0027	,1015	+ .0015

[a] Methods of preparation:

(1) Gattermann, Ber., 32, 1141 (1899); (2) Stewart, J. Chem. *Soc.*, **122**, 2557 (1922); (3) Krishna, *ibid.*, 123,157 (1923); (4) Autenrieth, Ber., 36,189 (1903).

Estimation of Fe^{+++} in Ferric Chloride Solution by Means of Sulfinic Acids.—A known volume of ferric chloride solution was taken and titrated against a standard sulfinic acid solution in the presence of dilute hydrochloric acid (orange-yellow precipitate of ferric sulfinate settled down). A dilute solution of potassium sulfocyanide was used as an external indicator, the end-point being detected when a drop of the solution gave no red coloration with the sulfocyanide solution, the test being performed on a glazed tile. Knowing the volume of the sulfinic acid solution required for a given volume of ferric chloride solution, the amount of iron per liter can be calculated according to the equation given above. Similar results were obtained with all the sulfinic acids used in this work, and for the sake of brevity the results of only a few typical ones are recorded below. The error ranges from 0.0001 to 0.0004 g. of Fe^{+++}, with

TABLE II

TITRATION OF FERRIC CHLORIDE SOLUTIONS

Standard Sulfinic Acid Contained 10 g. of RSOOH per Liter

Fe^{+++} in 5 cc. of $FeCl_3$ soln., g.	0.0101	0.0202	0 0290	0.0402	0.0503	0.0606
Fe^{+++} found with benzene sulfinic acid, g.	0 0100	0 0201	0 0289	0.0401	0.0502	0.0605
Fe^{+++} found with p-toluene sulfinic acid, g.	0 0102	0.0203	0.0291	0.0404	0.0505	0.0609
Fe^{+++} found with *p*-dichlorosulfinic acid, g.	0.0102	0.0203	0 0292	0.0403	0.0504	0.0606
Fe^{+++} found with *p*-chloronitrobenzene sulfinic acid, g.	0.0106	0.0211	0 0306	0.0416	0.0500	0.0609

an abnormality of p-chloronitrobenzene sulfinic acid with 3% ferric chloride solution in which case the error is 0.0016 g.

Estimation of Fe^{++} in the Presence of Fe^{+++}.—A solution of ferrous chloride was prepared and the amount of iron per liter determined by titrating it against standard potassium dichromate solutions. Then a known volume of ferric chloride solution was added to a known volume of ferrous chloride solution. To this mixture excess of sulfinic acid solution was mixed so as to isolate ferric as orange-yellow ferric sulfinate. This was filtered, washed well and the filtrate titrated against standard potassium dichromate solution, and the amount of pe^{++} thus determined was compared with the known ferrous chloride solution. The concentration of the ferrous chloride solution found agreed with the known value to within the accuracy of the measurement (about 0.1%) with all the sulfinic acids that were tried.

Estimation of Fe^{+++} in the Presence of Fe^{++}.—To a known volume of ferric chloride solution a definite volume of standard ferrous chloride solution was added. The mixture was then titrated against sulfinic acid solution of known strength, using potassium sulfocyanide as a side indicator. Results are tabulated below.

TABLE III

ESTIMATION OF Fe^{+++} IN THE PRESENCE OF Fe^{++}

RSOOH Contained 10 G. of RSOOH per Liter

Fe^{+++} in 5 cc. of $FeCl_3$ solution, g.	Titrated with benzene sulfinic acid, Fe^{+++} found, g.	Titrated with 1-chloro-4-nitrobenzene-2-sulfinic acid, Fe^{+++} found, g.
0.0101	0.0100	0.0106
.0202	.0201	.0211
.0290	.0289	.0299
.0402	.0401	.0404
.0503	.0502	.0500
.0606	.0605	.0609

The results obtained with other sulfinic acids were similar to those given here. The presence of Fe^{++} seems to have no influence on the quantitative precipitation of ferric sulfinates.

Estimation of Fe^{+++} in the Presence of Al, Cr, Ni and Co.—The solutions of the chlorides of these metals were used. The experiments were performed in exactly the same manner as given in the case of the estimations of Fe^{+++} in the presence of Fe^{++}. The results for Al alone are tabulated below since other results were exactly similar.

The results are in agreement with the theory. Again the presence of aluminum, chromium, nickel and cobalt have no effect on complete precipitation of ferric sulfinates.

Ferric Sulfinates.—Many of these sulfinates are not recorded in the literature and, therefore, warrant a short description here. The ferric

TABLE IV

RESULTS FOR ALUMINUM

RSOOH Contained 10 g. of RSOOH per Liter

Fe^{+++} in 5 cc. of $FeCl_3$ soln., g.	Titrated with *p*-toluene sulfinic acid, Fe^{+++} found, g.	Titrated with *p*-dichlorobenzene sulfinic acid, Fe^{+++} found, g.
0.0101	0.0102	0.0102
.0202	.0203	.0203
.0290	.0291	.0292
.0402	.0404	.0402
.0503	.0505	.0504
.0606	.0609	.0606

sulfinates prepared are found to be insoluble in all the usual organic solvents. The analysis was conducted by dissolving the ferric sulfinates in strong hydrochloric acid and precipitating ferric hydroxide from this by means of ammonia. The ferric hydroxide was ignited to Fe_2O_3 and from this the percentage of Fe was calculated as given in the table below.

TABLE V

ANALYTICAL DATA OF FERRIC SULFINATES

Ferric salt	Formula	Fe calcd., %	Fe found, %
Benzene sulfinate[1]	$C_{18}H_{15}O_6S_3Fe$	11.68	11.56
p-Toluene sulfinate[1]	$C_{21}H_{21}O_6S_3Fe$	10.74	10.94
p-Dichlorobenzene sulfinate	$C_{18}H_9Cl_6O_6S_3Fe$	8.16	8.24
Chloronitrobenzene sulfinate	$C_{18}H_9Cl_3N_3O_{12}S_3Fe$	7.83	7.93
m-Benzoic acid sulfinate	$C_{21}H_{15}O_{12}S_3Fe$	9.16	8.94
p-Dibromobenzene sulfinate	$C_{18}H_9Br_6O_6S_3Fe$	5.87	5.73
p-Chlorobenzene sulfinate	$C_{18}H_{12}Cl_3O_6S_3Fe$	9.61	9.48
p-Acetanilide sulfinate	$C_{24}H_{24}O_9N_3S_3Fe$	8.61	8.52
Salicylic acid sulfinate	$C_{21}H_{15}O_{15}S_3Fe$	8.49	8.40
m-Benzene disulfinate	$C_{18}H_{12}O_{12}S_6Fe_2$	15.46	15.78
p-Cinnamic acid sulfinate	$C_{27}H_{21}O_{12}S_3Fe$	8.13	8.01

Summary

Sulfinic acid (RSOOH) reacts with the ferric salt solutions to form orange-yellow ferric sulfinates of the general formula $(RSOO)_3Fe$.

The experiments have shown that the formation of such compounds is quantitative. Taking advantage of this property of the —SOOH group, its method of estimation has been investigated on the lines mentioned in the experimental part.

The method employed gives satisfactory results and it is found that its application is possible even in the presence of other negative groups such as NO_2, OH and COOH in the molecule.

The method has been used in the isolation and estimation of ferric ions in the presence of ferrous ions and also in the presence of aluminum, chromium, nickel and cobalt, which share many of its properties with iron. This also simplifies the methods of estimation hitherto employed.

Different strengths of ferric chloride solutions seem to bring no difference in their behavior towards the sulfinic acid solutions.

LAHORE, INDIA

[CONTRIBUTION FROM THE UNIVERSITY CHEMICAL LABORATORIES, UNIVERSITY OF THE PUNJAB]

A QUICK METHOD FOR ESTIMATION OF HALOGENS IN CERTAIN ORGANIC COMPOUNDS

BY S. KRISHNA AND JOTI SWARUP

RECEIVED JUNE 29, 1927 PUBLISHED MARCH 7, 1928

Several methods are available for quantitative determination of halogens in organic compounds and these are employed when total halogen is to be estimated. But in compounds where two types of halogen atoms are present (as in chlorobenzene sulfonyl bromide) and the amount and proportion of each of these has to be determined some modification of the above methods has to be employed. When the two halogen atoms behave differently such quantitative determination becomes a comparatively easy matter. For example, in chlorobenzene sulfonyl bromide bromine is much more labile than chlorine and hence reacts differently with certain reagents. Based on this principle, Hirst and Macbeth[1] have developed a method of estimating labile halogen on reaction with hydrazine hydrate by measuring the volume of nitrogen evolved according to the equation

$$RSO_2NCl_2 + NH_2NH_2 \longrightarrow RSO_2NH_2 + N_2 + HCl$$

Sometimes an organic compound has to be prepared by a process that involves several stages of intermediate compounds and these intermediate compounds have to be analyzed in order to find their purity. The case in view is the preparation of chloronitrobenzene sulfinic acid ($Cl:NO_2:SO_2H$ 1:4:2) from the corresponding sulfonic acid by reduction of sulfonic chloride. The sulfonic chloride has to be analyzed every time it is prepared. The usual methods involve great length of time, and therefore need was felt for some rapid method of estimation of one of the elements in such compounds. The present communication describes a method of estimating quickly labile halogens in certain organic compounds.

Krishna and Das[2] have shown that Baumann and Kux's method[3] can be employed for the estimation of sulfinic group. It is assumed that sulfonic acids would also react in the same manner as sulfinic acids toward a mixture of potassium iodide and potassium iodate. Thus it becomes possible to estimate sulfonic chlorides, since these on hydrolysis give

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[1] Hirst and Macbeth, J. *Chem. Soc.*, 121,904 (1922).

[2] Krishna and Das, *J. Ind.* C. S., 1927, 367.

[3] Baumann and Kux, Z. anal. *Chem.*, 32,129 *(1893).*

sulfonic and hydrochloric acids. In the case of *p*-toluene sulfonic chloride, for instance, the reaction proceeds according to the following equations

$$6CH_3C_6H_4SO_2Cl + 6H_2O = 6CH_3C_6H_4SO_3H + 6HCl$$
$$6CH_3C_6H_4SO_3H + 5KI + KIO_3 = 6CH_3C_6H_4SO_3K + 3H_2O + 3I_2$$
$$6HCl + 5KI + KIO_3 = 6KCl + 3H_2O + 3I_2$$
$$6I_2 + 12KOH + 6H_2O_2 = 12KI + 12H_2O + 6O_2$$

so that the chlorine present in the compound is equivalent to one-half of the oxygen that is liberated. It is well known that such substances as sulfonyl chloride, acid chlorides, picryl chloride, etc., are characterized by the facility with which they undergo hydrolysis. In compounds like chlorobenzene sulfonyl bromide, therefore, bromine which is in labile condition can easily be removed as hydrobromic acid and estimated as shown above.

Such compounds as have a labile halogen and a nitro group (as *o*-chloronitrobenzene, picryl chloride, etc.) give higher values than are demanded by theory. This may be due to the fact that the nitrophenols which are liberated on hydrolysis behave as weak acids and therefore react to some extent with potassium iodide and iodate solutions. It has been shown by Conant and Kirner[4] that the halogen atom in ACH_2Cl is more reactive than ACl, where A is a phenyl group. An attempt was therefore made to estimate halogen in benzyl chloride by the present method but it was found that only about 90% of the halogen could thus be estimated. Benzal chloride, however, gave satisfactory results according to the equations

$$3C_6H_5CHCl_2 + 5KI + KIO_3 = 3C_6H_5CHO + 6KCl + 3I_2$$
$$3I_2 + 3H_2O_2 + 6KOH = 6KI + 3H_2O + 3O_2$$

Halogen substituted fatty acids as, for example, monochloro-acetic, monobromo-acetic, ethyl chloroformate, etc., gave results that were in accordance with the usual Kux's equation. Chloral hydrate gave higher results and this may be due to the fact that the aldehyde group present in chloral hydrate is partly oxidized to carboxyl group by hydrogen peroxide and the acid thus formed reacts with iodide and iodate, giving higher values. Substances like dichloro-ethylene, however, react in the usual manner, liberating an equal volume of oxygen.

The following factors are essential to the success of the experiment.

1. The approximate adjustment of the proportions in which the reagents are mixed. Three g. of potassium iodide, 0.3 g. of potassium iodate (acid free), 2 cc. of 3% hydrogen peroxide and 4 cc. of carbonate-free potassium hydroxide (1:1) gave the best results.

2. Adjustment of the various conditions at the time of mixing the potassium iodide and the potassium iodate with the organic substance. In some cases the compound had to be boiled with water before the addition

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[4] Conant and Kirner, THIS JOURNAL, 46, 232 (1924).

of the above reagents at room temperature, whilst in others the addition of the reagents had to be carried out in ice-cold solutions. The various conditions are mentioned in the experimental portion of the work.

Experimental

The apparatus as described by Baumann and Kux[3] was employed and adjusted for measurements as described in "The Methods of Quantitative Organic Analysis."[5] A known weight of the labile halogen compound (about 0.15 g.) was introduced into the outer vessel, A, with a solution of **3** g. of potassium iodide and 0.3 g. of potassium iodate. Into the inner vessel, B, was taken a freshly made and cooled mixture of 2 *cc.* of **3%** hydrogen peroxide and 4 cc. of potassium hydroxide.

The sulfonic iodide, bromides and chlorides used in this work were prepared according to Otto and Tröger.[6] The results for p-toluene

TABLE I

ESTIMATION OF IODINE IN *p*-TOLUENE SULFONIC IODIDE

Time Taken to Complete the Reaction, Thirty Minutes

I Experiment no.	II Weight of sulfinic iodide taken, *g*.	III Wt. of oxygen, *g*.	IV Wt. of oxygen equivalent to iodine present, g.	Corresponding. wt. of iodine, g.	Iodine found, %	Iodine calcd., %	Percentage error
1	0.1263	0.0144	0.0072	0.0569	45.06	45.01	+0.05
2	.1317	.0149	.0075	.0591	44.87	45.01	− .14
3	.1867	.0211	.0105	.0836	44.8	45.01	− .21
4	.1993	.0226	.0113	.0898	45.06	45.01	+ .05

TABLE II

ESTIMATION OF HALOGENS IN VARIOUS SULFONIC HALIDES

	Sulfonic halide	Halogen calcd., %	Halogen found, %	Error, %	Time taken to complete re- action, hours
1	p-Toluene sulfonic bromide	34.02	34.00	−0.02	1
2	p-Toluene sulfonic chloride	18 64	18.63	− .01	3
3	Chlorobenzene sulfonic bromide (bromine)	31.28	31.32	+ .04	1
4	Chlorobenzene sulfonic iodide (iodine)	41.96	41 86	− .10	0.5
5	Chlorobenzene sulfonic chloride (active chlorine)	16.82	1679	− .03	3
6	p-Methoxytoluene sulfonic bromide	30.17	30.14	− .03	1.5
7	*p*-Methoxytoluene sulfonic iodide	40.69	40.64	− .05	0.75
8	*p*-Methoxytoluene sulfonic chloride	16.11	16.09	− .02	3.5
9	Sulfonic chloride of benzoic acid	16.11	16.08	− .03	3.5

[a] The time taken to complete the reaction which is given in the last column of Tables II, III and IV is that at the end of which no more oxygen was evolved on longer standing. In cases where no time is given, the volume of oxygen did not become stationary even after a long time.

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[5] P. C. R. Kingscott and R. S. G. Knight, Longmans, Green and Co., London, 1914, p. **74.**

[6] Otto and Troger, *Ber.*, 24,478488 (1891).

sulfonic iodide are given in Table I as a typical case. The mean results with other sulfonic halides are recorded in Table II.

Table III

Estimation of Halogens in Acid Chlorides

	Name of substance	Halogen calcd , %	Halogen found, %	Error,	Time taken to complete reaction. hours
1	Benzoyl chloride	25.26	25 22	−0.04	0.75
2	Acetyl chloride	45 22	45 05	− .17	.5
3	Phthalyl chloride	34.97	34 93	− .04	2
4	*p*-Nitrobenzoyl chloride	19.13	2098	+1.85	..
5	o-Nitrobenzoyl chloride	19.13	21 18	+2 05	..

Table IV

Estimation of Halogens in Other Halogen Compounds

	Name of substance	Halogen calcd., %	Halogen found, %	Error, %	Time taken to complete reaction, hours
1	Benzyl chloride	28 06	25.30	−2.76	4
2	Benzal chloride	44.10	43 99	−0.11	0.75
3	Monochloro-acetic acid	37.56	37.47	− .09	3
4	Monobromo-acetic acid	57 55	57.46	− .09	2.5
5	Ethyl chloroformate	32 71	32.75	+ .04	3
6	Chloral hydrate	64.35	66.87	+2.52	..
7	Dichloro-ethylene	73.19	73.12	+0.07	3
8	Picryl chloride	14.34	28.89	+14.55	
9	*o*-Chloronitrobenzene	22.54	25.33	+2.79	

Summary

Kux's iodine method for the estimation of carboxyl group has been successfully used for the estimation of labile halogens in certain halogenated organic compounds. It is found to be inapplicable to those compounds where a nitro group or an aldehyde group is present in the compound. Benzyl chloride and chloral hydrate give unsatisfactory results.

The method can also be used for the estimation of one of the halogen atoms in compounds that contain two different halogen atoms, one of which is present in the labile state, as in chlorobenzene sulfonic iodide.

Lahore, India

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

ARYLSULFONYLMAGNESIUM CHLORIDES AND THEIR REACTIONS WITH DIETHYL SULFATE

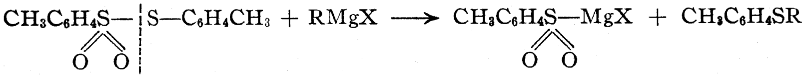
BY HENRY GILMAN AND ROBERT E. FOTHERGILL

RECEIVED JUNE 29, 1927 PUBLISHED MARCH 7, 1928

Introduction

Diethyl sulfate has been recommended[1] and used[2] as a reagent for characterizing intermediate compounds formed in reactions involving organometallic compounds. By means of this ester it is possible to replace an -MgX group by the ethyl group and thereby obtain a stable compound that lends itself to ready identification. This replacement reaction occurs with all -CMgX compounds studied, even when the quantity of RMgX compound present is very small.'' It is also generally applicable with -NMgX compounds, and with -SMgX compounds where the sulfur is bivalent. Unfortunately it has a very limited application with -OMgX compounds. The same type of replacement reaction is observed with other dialkyl sulfates and with alkyl and halogen alkyl esters of arylsulfonic esters.[3]

The -OMgX compounds, however, are not the only ones that have but a limited application in such replacement reactions. Gilman, Smith and Parker,[4] in connection with the proof of structure of the so-called disulfoxides, have shown that these compounds are true thiosulfonic esters and react as follows with RMgX compounds.



$$CH_3C_6H_4\underset{O\;\;O}{S}{-}\,|\,S{-}C_6H_4CH_3 + RMgX \longrightarrow CH_3C_6H_4\underset{O\;\;O}{S}{-}MgX + CH_3C_6H_4SR \qquad (I)$$

In that study the reaction product was heated with diethyl sulfate, prior to hydrolysis, in order to further establish the constitution of the thiosulfonic ester and its mode of reaction with RMgX compounds. However, the diethyl sulfate was apparently without reaction, for no ethyl *p*-tolyl sulfone was obtained from the p-tolylsulfonylmagnesium halide. Inasmuch as there exists no reasonable doubt concerning the correctness of Reaction I, it must follow that diethyl sulfate is unsuitable for replacing the -MgX group attached to hexavalent sulfur. Admittedly there is the possibility that the p-tolylsulfonylmagnesium halide underwent the following rearrangement.

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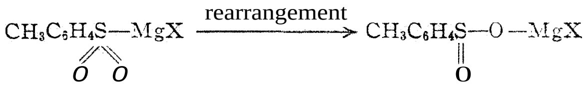
[1] Gilman and Hoyle, THIS JOURNAL, 44, 2621, 2969 (1922)

[2] (a) Gilman and Kinney, *ibid.*, 46, 493 (1924); (b) Gilman and Kirby, *ibid.*, 48, 1733 (1926).

[3] Gilman, Robinson and Beaber, *ibid.*, 48, 2715 (1926). References to earlier work are given in this paper.

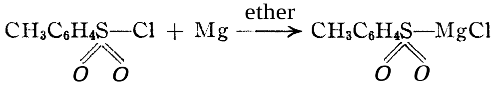
[4] Gilman, Smith and Parker, *ibid.*, 47, 851 (1925). See, also, the extensive work of Smiles and co-workers, particularly the paper by Miller and Smiles, J. Chem. *Soc.*, 127, 224 (1925).



$$CH_3C_5H_4\underset{O\ \ O}{S}—MgX \xrightarrow{\text{rearrangement}} CH_3C_6H_4\underset{\overset{\|}{O}}{S}—O—MgX \qquad (II)$$

There is no ready and exact method for differentiating between the two isomers in Reaction II. For one thing, hydrolysis throws no light on the solution of this problem inasmuch as the product formed is *p*-toluenesulfinic acid, a compound that has been interpreted by some as containing hexavalent sulfur ($CH_3C_6H_4\underset{O\ \ O}{S}—H$) and by others as having tetravalent sulfur ($CH_3C_6H_4\overset{\overset{O}{\|}}{S}—OH$). A third group maintains that we are dealing here with an equilibrium mixture of the two.

Whatever may be the structure, it is obvious that partial or complete rearrangement will give an -OMgX compound, and only a very limited number of such compounds[2"] undergo replacement reactions with diethyl sulfate. In order to have more facts for a possible solution of this problem, a study has been made of the direct reaction between arylsulfonyl chlorides and magnesium in ether. There is no question concerning the structure of compounds like benzenesulfochloride and *p*-toluenesulfochloride. If reaction occurs with magnesium, it should very probably take place as follows.



$$CH_3C_6H_4\underset{O\ \ O}{S}—Cl + Mg \xrightarrow{\text{ether}} CH_3C_6H_4\underset{O\ \ O}{S}—MgCl \qquad (III)$$

The recent work of Tistchenko[5] is related to this study. He showed that carboxylic acid bromides react with magnesium to give acylmagnesium bromides (RC(=O)MgBr).

Reaction has been found to occur between arylsulfonylchlorides and magnesium in ether. Hydrolysis of these new organomagnesium halides gives the corresponding sulfinic acids. Analysis shows them to be arylsulfonylmagnesium chloride-etherates. However, they do not give the corresponding ethyl sulfones when treated with diethyl sulfate. From this, and earlier work,[2"] it may be concluded that the -MgX group attached to sulfur as in a sulfonyl group is not replaceable by an ethyl group when diethyl sulfate is used. Over and against such a conclusion is the possibility that we may be dealing here with an -OMgX compound formed by a rearrangement like that illustrated in Reaction II. The possibility of such a rearrangement is reduced when one considers the conditions of the experiments and unpublished data that have shown diethyl sulfate to be reliable with even those RMgX compounds that are known at times to undergo rearrangement.[6]

[5] Tistchenko, Bull. *soc. chim.*, 37, 623 (1925).

[6] Mr. J. E. Kirby has shown that diethyl sulfate gives normal products with benzylmagnesium chloride, diphenylmethylmagnesium chloride and α-naphthylmethylmagnesium chloride.

Experimental Part

Benzenesulfochloride and Magnesium.—A solution of 35.3 g. (0.2 mole) of benzenesulfochloride in 100 cc. of dry ether was added slowly to 4.9 g. (0.2 mole) of magnesium turnings contained in a 500cc. three-necked flask fitted with a reflux condenser, stirrer and dropping funnel. The reaction was started by means of a crystal of iodine and by warming the reaction flask slightly. A slow reaction took place and the rest of the benzenesulfochloride solution was added over a period of one hour, during which a yellow precipitate formed. After refluxing for one-half hour and stirring at room temperature for twelve hours, the reaction mixture was hydrolyzed with water and 10% hydrochloric acid and then the ether and water layers were separated. The ether layer was extracted with 5% sodium hydroxide and then dried over anhydrous sodium sulfate and distilled at atmospheric pressure to remove the ether. The residue from this distillation was then vacuum distilled and gave 18.8 g. (53.2%) of unused benzenesulfochloride, b. p. 106–108° at 9 mm. (identified by the amide which melted at 152°). The sodium hydroxide extract was acidified and extracted with ether; this extract was dried over anhydrous sodium sulfate and then the ether was evaporated rapidly, leaving 3.5 g. (12.3%) of benzenesulfinic acid, m. p. 83°.

Benzenesulfochloride **and** Magnesium **and Ethyl** Sulfate.—In this experiment 35.3 g. (0.2 mole) of benzenesulfochloride in 150 cc. of dry ether was treated with 4.9 g. (0.2 mole) of magnesium under the conditions described in the preceding experiment except that the reaction was started with about 2 g. of activated[7] magnesium. The reaction mixture was refluxed for thirteen hours, then most of the ether was distilled off and 200 cc. of dry toluene added. Thirty and eight-tenths g. (0.2 mole) of diethyl sulfate was then added and the mixture refluxed for eight hours. After standing at room temperature for eighteen hours the reaction mixture was hydrolyzed with 10% hydrochloric acid. The ether layer was extracted with 5% sodium hydroxide and then steam distilled. The residue, not volatile with steam, was a yellow, oily liquid which did not crystallize on cooling to −12° or by slow evaporation of its ether solution. From the distillate were obtained by ether extraction and vacuum distillation 3.1 g. of a liquid boiling from 90 to 105° at 11 mm., probably a mixture of toluene and benzenesulfochloride, and 1.5 g. (4.3%) of unused benzenesulfochloride, boiling from 105 to 120° at 11 mm. (identified by a mixed melting point determination with a known sample of benzenesulfonamide). The sodium hydroxide extract yielded 0.7 g. (2.5%) of benzenesulfinic acid, m. p. 81°. No ethylphenylsulfone was obtained.

***p*-Toluenesulfochloride** and Magnesium.—In an experiment using 57.8 g. (0.3 mole) of p-toluenesulfochloride in 250 cc. of dry ether and 7.3 g. (0.3 mole) of magnesium, carried out under the same conditions as the first benzenesulfochloride experiment, 55.1 g. (95.0%) of the *p*-toluenesulfochloride was recovered, but no p-toluenesulfinic acid was obtained. In another experiment, 38.1 g. (0.2 mole) of *p*-toluenesulfochloride and 4.9 g. (0.2 mole) of magnesium were used. The reaction was started with about 2 g. of *activated*[7] magnesium and after all of the *p*-toluenesulfochloride was added the reaction mixture was refluxed for ten hours and then stirred at room temperature for ten hours

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[7] This activated magnesium was prepared according to the directions of Gilman, Peterson and Schulze from a powdered magnesium-copper alloy containing 12.75% of copper. A preliminary account of this superior activated magnesium was given at the Philadelphia Meeting of the American Chemical Society in September, 1926. Subsequent mention of it has been made in papers by Hurd and Webb, THIS JOURNAL, 49, 546 (1927), and Gilman and Harris, *ibid.*, 49, 1825 (1927). Details of this catalyst are given in a paper by Gilman, Peterson and Schulze to be published early in 1928 in *Rec. trav. chim.*

more. The products obtained after hydrolysis and the general procedures outlined above were 3.0 g. (5.2%) of unused p-toluenesulfochloride and 21.7 g. (69.5%) of *p*-toluenesulfinic acid, m. p. 88°. The identity of p-toluenesulfinic acid was confirmed by a mixed melting point determination made with an authentic specimen.

***p*-Toluenesulfochloride** and Magnesium and Ethyl Sulfate.—Thirty-eight and one-tenth g. (0.2 mole) of p-toluenesulfochloride was added to 4.9 g. (0.2 mole) of magnesium turnings in the same manner as the preceding experiment, using activated magnesium to start the reaction. After the reaction mixture had been refluxed and stirred for nine hours and then stirred at room temperature for eleven hours, about half of the yellow precipitate which had formed was filtered out of the reaction mixture and washed thoroughly with dry ether. Most of the ether was distilled from the remaining reaction mixture and then 200 cc. of dry toluene was added. Twenty-three and one-tenth g. (0.15 mole) of ethyl sulfate was then added and the mixture refluxed for eight hours. From the sodium hydroxide extraction after hydrolysis there was obtained **3.0** g. of p-toluenesulfinic acid, m. p. 85° (mixed melting point with an authentic specimen of p-toluenesulfinic acid was 87°). The residue, not volatile with steam, was dissolved in ether and allowed to concentrate slowly. At first a few crystals (m. p. 200°) formed and these were removed. Then, in about two weeks, 1 g. of *p*-tolyl-*p*-toluenethiosulfonate, m. p. 77°, was obtained (this was identified by a mixed melting point determination with a known sample of the thiosulfonic ester). The only product recovered from the steam distillate was a small amount of unused p-toluenesulfochloride. No ethyl-p-tolylsulfone was obtained.

The yellow precipitate which was filtered out of the reaction mixture prior to treatment of the other half with diethyl sulfate, was carefully dried in a desiccator over calcium chloride and analyzed.

Anal. Calcd. for $CH_3C_6H_4SO_2MgCl.(C_2H_5)_2O$: Cl, 12.27. Found: 12.24, 12.22.

Ether (by loss in weight on heating at 110°). Calcd.: 25.7%. Found: 26.17,.

The compound gave a qualitative test for magnesium. When hydrolyzed by dilute hydrochloric acid it gave p-toluenesulfinic acid, which was identified by a mixed melting point determination with an authentic specimen.

The arylsulfonylmagnesium chlorides do not give the Gilman and Schulze[8] color test for RMgX compounds. This is as one would expect, inasmuch as a positive color test is not shown by compounds having the -MgX group attached to sulfur or to oxygen.

Summary

Arylsulfonylmagnesium chloride etherates are formed when benzenesulfochloride and p-toluenesulfochloride are treated with magnesium in ether. Diethyl sulfate did not replace the -MgCl group in these compounds by an ethyl group.

AMES, IOWA

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[8] Gilman and Schulze, THIS JOURNAL, 47,2002 (1925).

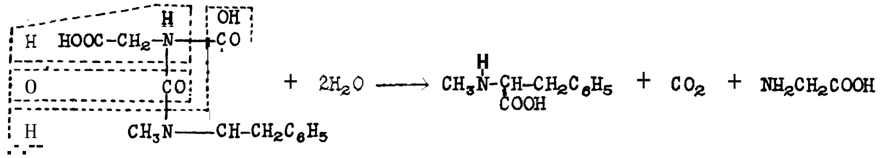
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

SYNTHESIS OF THE POLYPEPTIDE HYDANTOIN GLYCYL N-3-METHYLPHENYLALANINE HYDANTOIN[1]

BY DOROTHY A. HAHN AND JANET EVANS

RECEIVED JULY 23, 1927 PUBLISHED MARCH 7, 1928

The term polypeptide hydantoin was first applied by T. B. Johnson to cyclic urea combinations of a-amino acids.[2] Such substances may be distinguished from polypeptide combinations by the fact that while the latter undergo hydrolysis to give a-amino acids exclusively, the former give a-amino acids and carbon dioxide. A number of combinations of this type have been synthesized and their properties studied.[3] The present investigation was undertaken with a view to extending the knowledge of this class of compounds and also incidentally to work out a new method of preparation for the amino acid, α-N-methyl-β-phenylpropionic acid. This substance had previously been synthesized by E. Friedmann and S. Gutman[4] from α-bromo-β-phenylpropionic acid. It has now been prepared by decomposing the polypeptide hydantoin (a) N-3-methyl-4-benzyl-hydantoin-N-1-acetic acid and (b) N-1-N-3-dimethyl-4-benzylhydantoin under the action of barium hydroxide, as follows.



In a similar manner dimethylbenzylhydantoin (b) hydrolyzes to give α-N-methyl-β-phenylpropionic acid and methylamine. In each case the product was identified by comparison with the same acid obtained by synthesis according to Friedmann and Gutman's method. The preparation and the various chemical relationships of the above respective polypeptide hydantoins will now be considered separately.

The esters of N-3-methyl-4-benzyl-hydantoin-N-1-acetic acid were prepared by starting with ethyl-4-benzalhydantoin-N-1-acetate.[5] In repeating the work of Bates it has been possible to confirm his observation in regard to the existence of two geometrically isomeric forms of benzalhydantoin.[6]

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[1] This work is being offered in partial fulfilment of the requirements for the degree of Master of Arts at Mount Holyoke College

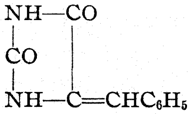
[2] Johnson, *Proc. Nat. Acad Sci.*, 2, 69 (1916).

[3] (a) Johnson and Bates, THIS JOURNAL, **38,** 1087 (1916); (b) Johnson and Hahn, *ibid.*, 39, **1255** (1917); (c) Hahn and Renfrew, *ibid.*, 47, 147 (1925); (d) Hahn and Gilman, *ibid.*, 47,2941 (1925)

[4] Friedmann and Gutman, *Biochem. Z.*, **27,** 491–497 (1910).

[5] Ref. **3** a, p. 1092.

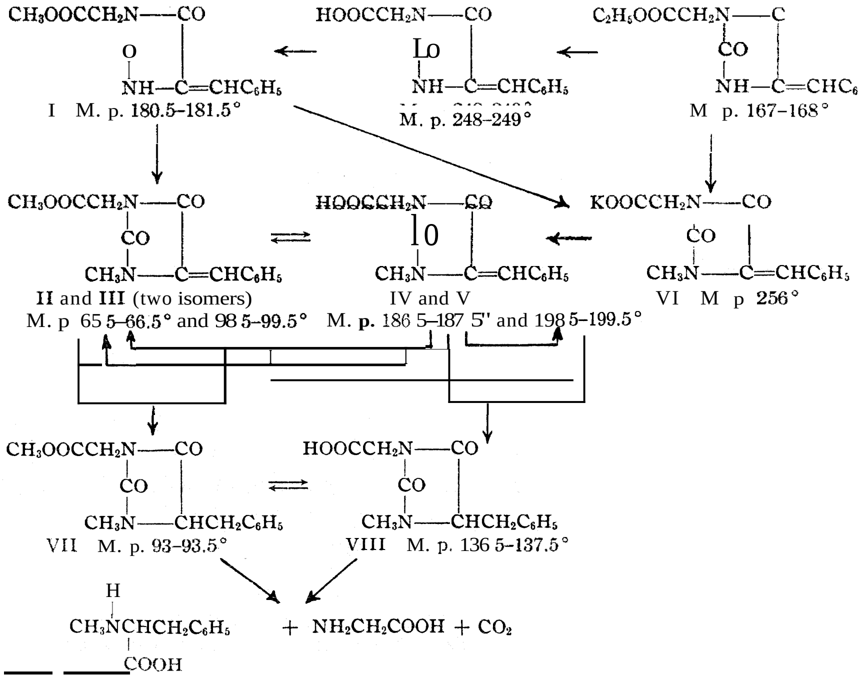
[6] Johnson and Bate.;, THIS JOURNAL 37, 384 (1915).



Curves showing the absorption spectra of these two compounds will be found included in this paper (Fig. 1). The existence of isomeric modifications belonging to the class of unsaturated hydantoins in which neither hydrogen atom nor the nitrogen has been substituted is thus demonstrated and the supposition[3d] is therefore no longer tenable that this kind of isomerism occurs only among unsaturated hydantoins in which the lability of the molecule has been decreased by the substitution of both free hydrogen atoms.

The preparation of methyl-N-3-methyl-4-benzalhydantoin-N-1-acetate, II and III, could not be effected to advantage in the usual way[7] since the yields were very low.

A better method was found to consist in alkylating the N-3-potassium derivative of potassium 4-benzalhydantoin-N-1-acetate. The substance, VI, obtained in this way was formed in good yield and was relatively quite pure. It was, therefore, used as the starting point in the preparation of the great majority of the derivatives of the hydantoins which are shown on the accompanying chart.



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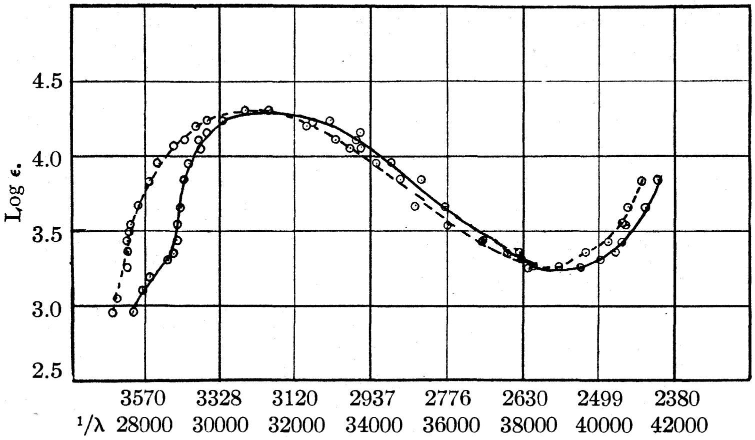
[7] Johnson and Nicolet. *Am. Chem.* J.,47, 468 (1913)

Potassium-N-3-methyl-4-benzalhydantoin-N-1-acetate, VI, passes into the lower-melting isomer of the corresponding acid, IV, when its aqueous solution is acidified. This acid, IV, isomerizes to give the higher-melting modification, V, when dissolved in aqueous acetic acid and subjected to the action of hydrogen chloride. The same acid, IV, when suspended in alcohol and the solution treated with gaseous hydrogen chloride passes into the corresponding higher-melting ester III. In order to obtain the lower-melting ester, II, it was necessary to esterify potassium N-3-methyl-4-benzalhydantoin-N-1-acetate, VI, by treating it with (a) dimethyl sulfate in an alkaline medium, (b) with methyl iodide in alcohol solution or (c) by treating its silver salt with methyl iodide. The product which was obtained in this way is exceedingly unstable and decomposes on standing with the formation of benzaldehyde. Both esters, II and III, reduce to give the same product, VII, when treated with hydrogen. The corresponding isomeric acids, IV and V, behave similarly, being transformed into the saturated acid, VIII. Other minor interrelationships are indicated on the chart. The constitution of the polypeptide hydantoin VIII, and, therefore, the constitution of all interrelated products, was established by the fact that under the action of barium hydroxide it may be hydrolyzed to give carbon dioxide glycine and α-N-methyl-β-phenylpropionic acid. Curves showing the absorption spectra of I, VII, IV and V will be found in Figs. 2 and 3.[8]



——— Benzalhydantoin, m.p. 215–216°C. – – – – Benzalhydantoin, m.p. 243–246°C.

Fig. 1.

Although the hydrolysis of the polypeptide hydantoin may be said to establish its constitution and the constitution of substances directly

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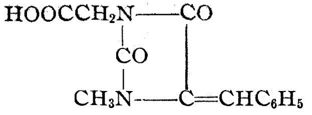
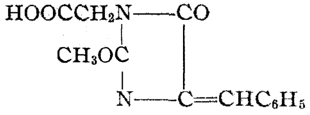
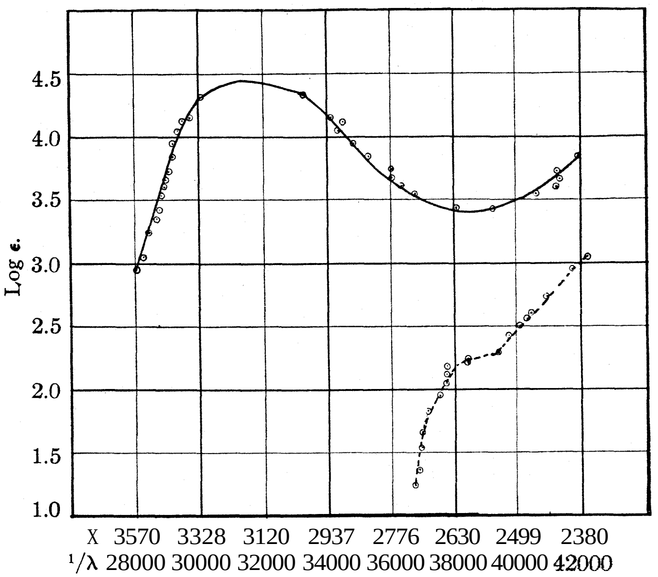
[8] Acknowledgment is made to Dr. Emma P. Carr for advice and assistance in the spectrographic work, which was done with the Hilger Quartz Spectrograph, E 36.

related to it, the possibility, nevertheless, presented itself that tautomeric equilibrium between the forms


(a)


(b)

might exist and that desmotropic modifications corresponding to these formulas might be assumed to represent the lower- and high-melting isomeric acids, IV and V. In order, therefore, to determine the presence



I ———— Methyl-4-benzalhydantoin-N-1-acetate, m.p. 180.5–181.5°C. VII – – – Methyl-N-3-methyl-4-benzylhydantoin-N-1 acetate, m.p. 93–93.5°C.

Fig. 2.

of any appreciable quantities of an enol form (b), Zeisel determinations were run on both isomeric acids. The results showed that while traces of methyl were split off from the higher-melting isomer[9] (about 2% of the total methyl), the quantity of the enol modification which might be present at any time would not be sufficient to account for the observed phenomenon of isomerization between the two forms.

In conclusion emphasis must be placed on the fact that in the case of the isomeric esters II and III, the lower-melting modification is by far the more unstable, while in the case of the isomeric acids IV and V the

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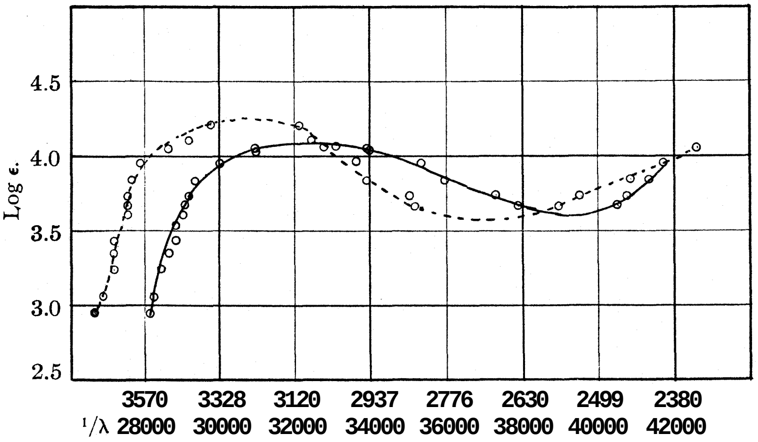
[9] Goldschmiedt reports numerous instances in which methyl groups have been observed to split off from nitrogen at a low temperature. Compare *Monatsh.*, 27, 849–878 (1906).

reverse holds true and the lower-melting modification represents the stable form. Such a marked difference in the stability of any two isomeric modifications has never before been observed in this series although a fairly large number of such pairs of compounds have been prepared and studied.[10] In the case of the substances under consideration the lower-melting ester (m. p. 65°) is so unstable that even the purest crystalline specimens, although perfectly dry and apparently free from solvent, slowly change into an oil under the action of light. This change is accompanied by the splitting off of benzaldehyde and the formation of a solid product which is characterized by the fact that it has a relatively high melting point (around 278°) and that it is extremely insoluble in ordinary solvents.



IV ——— N-3-Methyl-4-benzalhydantoin-N-1-acetic acid, m.p. 186.5–187.5°C. **V** - - - - N-3-Methyl-4-benzalhydantoin-N-1-acetic acid, m.p. 198.5–199.5°C.

Fig. 3.

The higher-melting isomeric ester does not melt to an oil upon standing but it suffers a change in melting point from 98.5–99.5° to 97–245°. In recrystallizing the mixture which has formed in this way, it is relatively easy to recover the pure ester by filtering its alcoholic solutions from minute quantities of the same insoluble, high-melting products (that is, m. p. 278°). The transformation to this insoluble product is most readily followed in the case of either isomer by allowing a solution of the substance in alcohol or ether to stand in the sunlight or better in a quartz flask under the ultraviolet rays of a mercury lamp. Under these conditions the solution which was originally perfectly clear and transparent begins to show the formation of an extremely light, flocculent precipitate. The formation of the precipitate continues steadily, under the action of ultra-

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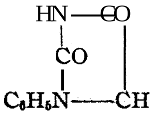
[10] Ref. 3 d, p. 2953.

violet light, and appears to represent a time reaction. Solutions of the isomeric acid, V, behave similarly but in this case the resulting insoluble product melts even higher, m. p. 292°.

The splitting off of benzaldehyde from the ester, m. p. 65.5°, has been definitely established and in this connection it is interesting to note that the amount of affinity on the methylene carbon atom in the 4-position which may be exercised in holding various substituents in the hydantoin ring, seems to be very decidedly affected by the substitution of hydrogen in the N-3-position. Thus, for example, it has been observed that hydantoins which contain phenyl groups in the **N-3** position, namely



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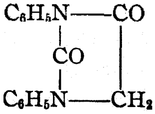

will not react with benzaldehyde nor with anisaldehyde,[11] and that in general substitution in this position decreases the reactivity of the methylene hydrogen.[12] It is now found that substituents in the 4-position tend to split off in the case of hydantoin derivatives which also contain substituents in the N-3-position. A more detailed account of the products which result from the decomposition of the isomeric unsaturated acids and esters under the action of light is given in a separate paper (see THIS JOURNAL 49,2877 (1927)).

Experimental

Ethyl-4-benzalhydantoin-N-1-acetate was used as the starting point in the present investigation. This substance had been prepared by the alkylation of benzalhydantoin.[11a,5] In repeating this work it has been possible to confirm the discovery by Johnson and Bates[6] of the existence of two isomeric forms of benzalhydantoin. The higher-melting modification, m. p. 246°, could be detected only in handling large quantities of this material since it is present in very small quantities. It is much less soluble in any given solvent than the lower-melting modification m. p. 215–216.[13] Both substances were analyzed and their absorption curves plotted. It is interesting to note that the absorption spectra of these two substances bear somewhat the same general relationship to each other as has been observed in the case of isomeric modifications of N-1-N-3-di-substituted hydantoins.

The existence of isomeric modifications of ethyl-4benzalhydantoin-N-1-acetate was not confirmed although large quantities of material were handled and a careful search was made of all residues. In this connection it may be said that the most convenient method for separating ethyl-4-

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[11] (a) Wheeler and Hoffman, *Am.* Chem. *J.*, 45,371 (1911) and (b) ref. **3** a, p. 1093.

[12] Johnson and Renfrew (not yet published).

[13] Compare Wheeler and Hoffman, m. p. **220°** (ref. 11 a).

benzalhydantoin-N-1-acetate from benzalhydantoin was by extraction with boiling chloroform, in which solvent the latter substance is practically insoluble.

In preliminary experiments undertaken with a view to substituting methyl for hydrogen in the N-3-position by the usual procedure of treating ethyl-4benzalhydantoin-N-1-acetatefirst with an equivalent of potassium hydroxide in alcohol solution and then with methyl iodide, it was found that the resulting product consisted of a very bad mixture. In order to eliminate complications which might arise as the result of a possible interchange of ethyl and methyl groups during the course of this reaction, ethyl-4-benzalhydantoin-N-1-acetate was, therefore, transformed into the corresponding methyl ester before alkylation with methyl iodide.

Methyl-4-benzalhydantoin-N-1-acetate, I, was prepared by transforming the corresponding ethyl ester into the potassium salt. One hundred g. dissolved in 1200 cc. of boiling alcohol and treated with 30 g. of potassium hydroxide (1.3 equivalents) in 200 cc. of boiling alcohol, yielded 110 g. of pure salt. This salt was completely soluble in cold water and its aqueous solution when acidified with hydrochloric acid gave quantitative yields of the corresponding acid, m. p. 248–249°.[14] The acid, when suspended in methyl alcohol and the solution saturated with dry hydrogen chloride gas, passed quantitatively into the corresponding methyl ester, m. p. 180.5–181.5° (I).

Anal. Calcd. for $C_{13}H_{12}O_4N_2$: N, 10.77. Found: 10.47. 10.58.

The ester is slightly soluble in cold methyl alcohol (1.3 g. in 200 cc.) but somewhat more soluble in the boiling solvent (1 g. in 40 cc.) from which it separates on cooling in long, white needles which completely fill the space occupied by the solution. Its absorption spectrum corresponds very closely to that of the unsubstituted benzalhydantoin.

Methyl-N-3-methyl-4-benzalhydantoin-N-1-acetate, II and III, m. p. 65.5–66.5° and 98.5–99.5°. Two isomeric esters which correspond to the above melting points have been isolated. Of these the lower-melting modification is the more soluble. A mixture of the two isomers was obtained by dissolving 10 g. of methyl-4-benzalhydantoin-N-1-acetate in methyl alcohol and treating the solution first with an equivalent of potassium hydroxide in alcohol solution and then with the calculated quantity of methyl iodide. The solution was heated on a water-bath until neutral to litmus and then set aside to cool. Successive crystalline precipitates were identified as unacted upon methyl-4-benzalhydantoin-N-1-acetate, the corresponding potassium salt, the potassium salt of N-3-methyl-4-benzalhydantoin-N-1-acetate and the corresponding methyl ester, m. p. 65.5–66.5°. In all a maximum yield of about 2 g. of the last named substance was obtained. An oily residue which refused to crystallize was assumed to consist of additional quantities of this ester mixed with its higher-melting isomer, since the oil when taken up in alcohol and subjected to the action of dry hydrogen chloride passed quantitatively into the pure crystalline ester, m. p. 98.5–99.5°. Since a fairly large number of test experiments, operated under different conditions of concentration and employing different quantities of potassium hydroxide, gave more or less identical mixtures which were tedious to separate this method of preparation was abandoned.

A much more convenient method consisted in methylating potassium-4-benzalhydantoin-N-1-acetate instead of either of its correspondingesters. This procedure was suggested by the fact that N-1-N-3-disubstituted hydantoins are very much more soluble than the corresponding N-1-mono-substitution products. Moreover, since potas-

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[14] Compare Johnson and Bates, m. p. 258° [This Journal, 38, 1094 (1916)].

sium-4-benzalhydantoin-N-1-acetate is almost insoluble in boiling methyl alcohol, it was hoped not only that the course of the reaction might be followed by its gradual disappearance but that the methylated product might be readily separated in pure condition. Both expectations were realized. The potassium N-3-methyl-4benzalhydantoin-N-1-acetate which was synthesized in this way will be described later. When an aqueous solution of this salt was treated with hydrochloric acid, the lower melting of the two isomeric forms of N-3-methyl-4-benzalhydantoin-N-1-acetic acid, IV (m. p. 186.5–187.5°), was obtained. Using the latter substance as a starting point, it was now possible to obtain either of the two isomeric esters by employing one or the other of the following modes of procedure.

Methyl-N-3-methyl-4-benzalhjdantoin-N-1-acetate, II, m. p. 65.5–66.5°, was prepared by esterifying the corresponding lower-melting acid, IV, in alkaline solution under the action of dimethyl sulfate.[15] The fact that the lower-melting ester was formed exclusively under these conditions would seem to strengthen the suspicion that this modification is stable only in neutral and alkaline media. Six grams of acid, m. p. 186.5–187.5°, was added to a solution of 1.2 g. of potassium hydroxide in 40 cc. of methyl alcohol. The resulting clear solution was then treated with the calculated quantity of dimethyl sulfate (6 cc.) which was added slowly through a dropping funnel under constant shaking and cooling in an ice-bath. After standing for two hours under occasional shaking in an ice-bath, solid potassium hydroxide was added in small quantities (total was 2–3 g.) under slight warming until the solution remained neutral. The resulting mixture was treated with enough cold water to dissolve the potassium methyl sulfate which had separated out in the form of fine crystals. The solution of this substance was followed, on the addition of further quantities of water, by the separation of methyl-N-3-methyl4-benzalhydantoin-N-I-acetate, m. p. 65.5–66.5°. The ester was purified by recrystallization from methyl alcohol.

This ester was also formed when 6.5 g. of N-3-methyl-4-benzalhydantoin-N-1-acetate was suspended in 10 cc. of alcohol and 15 cc. of methyl iodide and heated on a water-bath for twenty hours. The product obtained represented about 20% of the theoretical. It seems probable that the yield could be improved by varying the concentration of the methyl iodide in alcohol since the observation was made that with methyl iodide alone or with very dilute solutions of methyl iodide in alcohol, no reaction took place.

When 2.6 g. of the corresponding silver salt was treated with 10 cc. of methyl iodide diluted with 5 cc. of methyl alcohol, an immediate reaction took place and the ester was deposited in almost pure condition and quantitative yield.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: N, 10.21. Found: N, 10.16, 10.20.

The ester is very soluble in hot methyl alcohol (2 g. in 5 cc.) from which it separates on cooling in a freezing mixture in the form of rosets composed of fine, white needles or plates. The ester is very unstable and even when pure, dry and apparently free from all traces of solvent decomposes on standing into an oil which smells strongly of benzaldehyde. The period required for this transformation has varied from one week to six months. The ester passes readily and quantitatively into the corresponding higher-melting isomer when dissolved in methyl alcohol and treated with dry hydrogen chloride. It forms a mixture of the corresponding lower-melting acid and the open chain hydantoin acid on saponification with aqueous potassium hydroxide and subsequent acidification of the aqueous solution of the potassium salt. Reduction of the ester, II, to the corresponding saturated ester, VII, took place quantitatively under the action of hydrogen in the presence of palladium.

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[15] (a) Compare Ullmann and Wenner, Ber., 33, 2476 (1900); (b) Hans Meyer, *Ber.*, 37, 4144 (1904); (c) 40, 2432 (1907).

Methyl-N-3-methyl-benzalhydantoin-N-1-acetate, III, m. p. 98.5–99.5°, was prepared by dissolving the lower-melting modification of the corresponding acid in methyl alcohol and saturating the solution with dry hydrogen chloride gas. For example, 44 g. of crude acid (m. p. 176–181°) was dissolved in 200 cc. of methyl alcohol and the solution saturated with dry hydrogen chloride. After saturation the mixture was refluxed on a steam-bath and then cooled and resaturated with hydrogen chloride This process was repeated until the crystalline ester separated out from the solution on cooling. In cases where the filtrate from these crystals deposited an oil after concentrating and cooling, the oil was taken up in alcohol, resaturated with hydrogen chloride, etc. In this way a complete transformation of the lower-melting acid, IV, into the higher-melting ester, III, was effected and a theoretical yield of the desired product was obtained. **Methyl-N-3-methyl-4-benzalhydantoin-N-1-acetate** was also prepared from the higher-melting isomeric acid, V, and from the lower-melting ester, II, by the application of the above general method of procedure.

Anal. Calcd. for $C_{14}H_{14}O_4N_2$: N, 10.21. Found: 10.16, 10.19.

The ester is very soluble in hot methyl alcohol (1 g. in 7 cc.) from which it crystallizes on concentrating the solution or upon precipitation by the addition of water. The purification is most readily effected by recrystallization from concentrated alcohol solutions from which it separates in rosets consisting of pale yellow needles or plates. When reduced by hydrogen in the presence of palladium it passes quantitatively into the corresponding saturated ester, VII. On hydrolysis it passes quantitatively into the corresponding high-melting acid, V.

It was never observed to pass into an oil on standing but did suffer a gradual change in its melting point, from 98–99° to 97–245°. This change resulted from the partial decomposition of the ester into a white substance, m. p. 276–278°, which is insoluble in alcohol and which can, therefore, be separated readily from the undecomposed ester by recrystallizing the latter from alcohol.

Potassium-N-3-methyl-4-benzalhydantoin-N-1-acetate, VI, m. p. 255–256°, was prepared by treating potassium-4-benzalhydantoin-N-1-acetate in 10 g. portions with 1.3 equivalents of potassium hydroxide in alcohol solution. The mixture was heated on a water-bath until the solution was perfectly clear and the transformation to potassium N-3-potassium-benzalhydantoin-N-1-acetate therefore complete. The calculated quantity of methyl iodide was then added and the heating continued at 65–70° for one and one-half hours or until the solution was neutral to litmus. The solution was then concentrated to small volume and the di-potassium derivative precipitated by the addition of ether. If, after concentrating the solution and cooling, the separation of small quantities of a crystalline precipitate was observed, this was removed by filtration before adding the ether, since it always represented traces of unacted upon potassium-4-benzalhydantoin-N-1-acetate. In cases where the methyl alcohol contained traces of acetone, iodoform was precipitated along with the condensation product. The latter was purified by recrystallization from alcohol. Since the purification of the salt when prepared in this way is complicated by the presence of iodoform and also of potassium iodide so that the yield approximated only about 50% of theory, it was found desirable to modify the procedure in the following way. Instead of precipitating the salt by the addition of ether to the concentrated solution of the reaction product, it was diluted with water and hydrochloric acid was added. Under these conditions the corresponding acid was precipitated in yields which vary between 80 and 90% of the theoretical. The acid so obtained reacted with potassium hydroxide in alcohol-water solutions to give the potassium salt in quantitative yields and pure condition. After two recrystallizations from hot methyl alcohol it was heated to constant weight and analyzed.

Anal. Calcd. for: $C_{12}H_{11}O_4N_2K$: N, 9.40. Found: 9.37, 9.32.

Silver-N-3-methyl-4-benzalhydantoin-N-1-acetate was prepared by treating alcohol solutions of the corresponding potassium salt with alcoholic silver nitrate.[16] The precipitated silver salt was dissolved by passing a stream of ammonia gas into the mixture, which was then filtered from silver oxide and the filtrate evaporated over sulfuric acid in a vacuum desiccator. After one recrystallization from boiling water it was analyzed.

Anal. Calcd. for $C_{13}H_{11}O_4N_2Ag$: N, 7.63. Found: 7.67.

The salt is soluble in boiling water (1 g. in 200 cc.) from which it separates on cooling in shining white crystals. It decomposes at 235" with the formation of a silver mirror. It passes into the corresponding acid, IV, when digested with aqueous potassium hydroxide and then acidified.

N-3-methyl-4-benzalhydantoin-N-1-acetic Acid.—Two isomeric forms of this substance, *viz.*, IV and V, m. p. 186.5–187.5° and 198.5–199.5°, were isolated. The lower-melting modification was obtained by treating the condensation product from potassium-4-benzalhydantoin-N-1-acetate with hydrochloric acid in the manner which has just been described. It was also prepared by acidifying aqueous solutions of pure potassium-N-3-methyl-4-benzalhydantoin-N-1-acetate, VI. After recrystallization first from methyl alcohol and then from acetone, it was found to have the following composition.

Anal. Calcd. for $C_{13}H_{12}O_4N_2$: N, 10.77. Found: 10.55, 10.59.

The acid is very soluble in boiling methyl alcohol (1 g. in 10 cc.), acetone (1 g. in 20 cc.) and acetic acid (1 g. in 20 cc.). It separates from these solutions on cooling in the form of small, transparent cubes or prisms. When dissolved in acetic acid, it passes under the action of hydrogen chloride into the higher-melting acid, V, and when dissolved in methyl alcohol and subjected to the same treatment, it passes into the corresponding methyl ester, III. Under the action of dimethyl sulfate in alkaline media it yields the lower-melting ester, II, and with hydrogen iodide it is reduced to the corresponding saturated acid, VIII.

The isomeric acid, V, m. p. 198.5–199.5°, was prepared by dissolving 11 g. of the lower-melting modification, IV, in a mixture of 200 cc. of acetic acid and 1000 cc. of concentrated hydrochloric acid. This solution when evaporated to small volume deposited the substance in pure condition. The acid may also be prepared by starting with higher-melting ester, III. Thus 2 g. of the ester, m. p. 98.5–99.5°, when dissolved in a mixture of 50 cc. of acetic acid and 25 cc. of concentrated hydrochloric acid and heated on a steam-bath in an open beaker for five hours, passed quantitatively into the higher-melting corresponding acid. When purified by recrystallization first from methyl alcohol and then from aqueous acetone, the substance gave abnormally low percentages of nitrogen on analysis. Such specimens when heated in an electric oven at 115° for twenty-four hours suffered a loss in weight which corresponded approximately to the loss of one molecule of water. (Calcd. % loss in weight for 1 mole of H_2O: 6.41. Found: 5.88, 6.03.) Other specimens of the acid which were recrystallized first from glacial acetic acid and then from pure, dry acetone when heated in the above manner suffered a loss in weight corresponding to 0.35 and 0.38% of water present. These specimens after heating gave the following results on analysis.

Anal. Calcd. for $C_{13}H_{14}O_4N_2$: N, 10.77. Found: 10.65, 10.63.

This acid is very soluble in boiling methyl alcohol (1 g. in 6 cc.), acetone (1 g. in 15 cc.) and acetic acid (1 g. in 12 cc.). It esterifies readily to give III when its methyl alcohol solution is treated with dry hydrogen chloride and like the corresponding lower-melting isomer, it passes into the saturated polypeptide hydantoin, VIII, on treatment with hydrogen iodide.

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[16] Compare Schaal, *Ber.*, 40, 4786 (1907).

Zeisel determinations were carried out in the case of both of the unsaturated isomeric acids, IV and V, with a view to ascertaining whether in either case the methyl group had shifted its position in the molecule from nitrogen to oxygen as the result of possible tautomeric rearrangements. The results were as follows: (1) no precipitate in the case of IV; (2) in the case of V, m. p. 196.5–198°, 0.3648 g. of acid gave 0.0085 g. of silver iodide; 0.3598 g. of acid gave 0.0068 g. of silver iodide. These results correspond to 0.15% and 0.12% of methyl, respectively. This may be assumed to be present (a) in combination with oxygen or (b) in loose combination with nitrogen.[17] Since the total percentage of methyl present in the molecule is equal to 5.77%, it follows that 0.5% and 0.2% has been split off in this process.

Methyl-N-3-methyl-4-benzylhydantoin-N-1-acetate, VII, m. p. 93–93.5°, was prepared by reducing the corresponding unsaturated esters, II and III, with hydrogen in the presence of palladium. It was also prepared by esterifying the corresponding acid, VIII, by saturating its methyl alcohol solution with hydrogen chloride. The method followed in reduction was the same as has been previously described in the case of ethyl-4-anisylhydantoin-N-1-propionate;[18] the reaction was quantitative and the resulting product practically pure. The substance was recrystallized from boiling methyl alcohol (1 g. soluble in 2 cc.) from which it separates in the form of large, rectangular prisms.

Anal. Calcd. for $C_{14}H_{16}O_4N_2$: N, 10.14. Found: 9.95, 9.99.

On hydrolysis with potassium hydroxide the ester passes quantitatively into the corresponding add VIII.

N-3-Methyl-4-benzylhydantoin-N-1-acetic Acid, VIII, m. p. 136.5–137.5°, was prepared by reducing the isomeric unsaturated esters II and III and the acids, IV and V, with hydrogen iodide in the presence of red phosphorus and also from the corresponding saturated methyl ester VII by saponification with potassium hydroxide. In the case of the isomeric unsaturated compounds the procedure was the same in all cases: 2 g. of substance. 0.5 g. of red phosphorus, 20 cc. of acetic acid and 5 cc. of hydrogen iodide (sp. gr. 1.70) were heated for two hours in a flask fitted with a short air condenser on an oil-bath at 120–130°. The solution was then evaporated almost to dryness on a steam-bath, 10 cc. of water added and the solution again evaporated. This process was repeated several times in order to remove traces of hydrogen iodide. The aqueous solution (about 20 cc.) was filtered hot from the red phosphorus and set aside to cool, when on seeding the acid separated in the form of very small, white prisms. Specimens obtained in this way were found in all cases to be identical.

Anal. Calcd. for $C_{13}H_{14}O_4N_2$: N, 10.69. Found: N, 10.65, 10.60.

The acid is soluble in boiling water (1 g. in 8 cc.) from which it is precipitated on cooling in the form of an oil which solidifies on standing. When present in less concentrated aqueous solutions (1 g. in 30 cc.) it separates on seeding in crystalline form. It is very soluble in acetic acid, methyl alcohol and acetone. Dissolved in methyl alcohol and treated with hydrogen chloride it passes readily and quantitatively into the corresponding ester, VII.

Hydrolysis of the Polypeptide Hydantoin N-3-Methyl-4-benzylhydantoin-N-1-acetic Acid, VIII.—The hydrolysis was conducted in the manner described in the case of 4-hydroxy-benzylhydantoin-N-1-propionate.[19] Thus 7.4 g. of acid was added to a flask containing 50 g. of barium hydroxide, 100 cc. of methyl alcohol and 100 cc. of water and heated on a steam-bath for three and one-half days. The product was filtered hot to remove solid barium hydroxide and barium carbonate and the alkaline filtrate exactly

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[17] Goldschmiedt, *Monatsh.*, 27, 849–878 (1906).

[18] Ref. 3 d, p. 2948.

[19] Ref. 3 d, p. 2951.

neutralized by the addition of sulfuric acid. The precipitated barium sulfate was filtered hot and extracted several times with small quantities of hot water. The filtrate and aqueous extracts were then combined and evaporated to small volume when successive precipitates of the undecomposed polypeptide hydantoin, VIII (about 3 g.) and α-N-methyl-β-phenylpropionic acid separated. The filtrate from these substances on further concentration was treated with absolute alcohol. The precipitate which formed in this way was suspended in absolute alcohol and the solution saturated with hydrogen chloride, when a crystalline substance was obtained which was identified as glycine ester hydrochloride. The experiment was then repeated and the polypeptide hydantoin digested with barium hydroxide over a longer period (eleven days). Under these conditions the decomposition was found to be complete and quantitative yields of α-N-methyl-β-phenylpropionic acid and glycine hydrochloride were obtained.

The a-N-methyl-p-phenylpropionicacid was identified by comparison with a specimen which was synthesized in the following way. Malonic ester was transformed into benzyl malonic ester'' and then into bromobenzyl malonic acid, which was purified by recrystallization from toluene.[21] The corresponding monobasic acid (a-bromo-p-phenylpropionicacid) was then prepared according to the method described by Fischer[22] and immediately transformed into the N-methylamino derivative by treatment with methyl amine.[4] The product was purified by crystallization from boiling water when it sublimed at 254°. Its identity was finally established by an analysis.

Dimethylbenzalhydantoin, m. p. 83–84', was used as the starting point for the preparation of a-N-methyl-p-phenylpropionic acid and was made in the usual way.[7] Benzalhydantoin[11a] was dissolved in a 50% aqueous alcohol solution of potassium hydroxide (1.2 equivalents) and then treated with the calculated quantity of methyl iodide. The product always consisted of a mixture of benzalhydantoin which separated on cooling in almost pure condition (m. p. 200–220°) and a new product (m. p. 70–90°) which separated on concentrating the filtrates. When 1.2 equivalents of potassium hydroxide were used, the yield of the latter substance approximated 30% of the theoretical but on increasing the amount of potassium hydroxide to 2.2 equivalents the yield was increased to 70%. This product was purified by extraction with cold chloroform (in which benzalhydantoin is almost insoluble) and subsequent recrystallization from alcohol. When pure it melted at 83–84°.

Anal. Calcd. for $C_{12}H_{12}O_2N_2$: N, 12.96. Found: N, 12.69, 12.74.

Dimethylbenzalhydantoin is soluble in boiling chloroform (45 g. in 100 cc.), cold 95% alcohol (5 g. in 100 cc.), boiling 95% alcohol (40 g. in 100 cc.) and boiling 50% alcohol (12 g. in 100 cc.). When crystallized from 95% alcohol solution and allowed to cool slowly, it forms large, transparent, rhombic plates. When treated with hydrogen iodide it is readily reduced to the corresponding dimethylbenaylhydantoin.

Dimethylbenzylhydantoin, m. p. 86.5–87°, was prepared by treating dimethylbenzalhydantoin, m. p. 83–84°, with hydrogen iodide (sp. gr. 1.7) in the presence of red phosphorus. The product was obtained in pure condition and in practically theoretical quantities. After three recrystallizations from methyl alcohol, its melting point was 86.5–87°. The fact that its melting point is so nearly the same as that of the corresponding unsaturated compound from which it was prepared led to a doubt as to whether reduction had actually taken place. This doubt was dispelled by melting the two substances together when a mixed melting point of 62–74" was obtained.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: N, 12.84. Found: N, 12.68. 12.73.

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[20] Conrad, Ann., 204, 174 (1880).

[21] Fischer, *Ber.*, 37, 3063 (1904).

[22] Ref. 21, p. 3064.

Dimethylbenzylhydantoin is soluble in hot methyl alcohol (**10** g. in **20** cc.) from which it crystallizes in transparent, rectangular prisms.

Hydrolysis of the Polypeptide **Hydantoin N-1,3-Dimethylbenzylhydantoin.**—The hydrolysis of dimethylbenzylhydantoin was accomplished by boiling 6 g. of the hydantoin with 50 g. of barium hydroxide for four days. The product was filtered from solid barium carbonate and barium hydroxide and then steam distilled into a flask containing hydrochloric acid. The distillate was evaporated to dryness and the residue recrystallized twice from absolute alcohol. When pure it was found to melt at **225–226.5°.** This product was shown to consist of the hydrochloride of methylamine, since its melting point was not lowered by melting with a sample of methylamine hydrochloride which had been prepared by neutralizing a 33% solution of methylamine[23] with hydrochloric acid.

The liquid remaining after steam distillation was exactly neutralized with sulfuric acid, filtered from the barium sulfate and concentrated. The crystals which precipitated on cooling were found to be identical with the α-N-methyl-β-phenylpropionic acid prepared from the acetic acid derivative and from malonic ester. Both methylamine hydrochloride and the amino acid were obtained in theoretical yield.

Summary

The amino acid α-N-methyl-β-phenylpropionic acid has been prepared by the hydrolysis of two different polypeptide hydantoins. The phenomenon of isomerization by the action of hydrochloric acid has again been observed in connection with the study of two separate pairs of geometric isomers. The tendency of substituents in the 4-position to split off when the N-3-position is occupied by a group other than hydrogen has been observed. This corresponds with observations already made as to the relative inactivity of methylene hydrogen in the 4-position toward carbonyl oxygen when this hydrogen is present in hydantoin compounds which contain substituents in the N-3-position.

Graphs showing the absorption spectra of isomeric forms of benzalhydantoin and of its N-3-methyl-N-1-acetic acid derivatives serve to confirm the theory that these pairs of isomers are of the geometric variety and also to emphasize the difference in the curves of isomeric substances in which the N-3-position is occupied and in which it is not.

SOUTH HADLEY, MASSACHUSETTS

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[23] Purchased from the Eastman Kodak Company, Rochester, New York.

[CONTRIBUTION FROM THE BAKER CHEMICAL AND ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF FLUORESCEIN, FLUORAN AND SOME RELATED COMPOUNDS[1]

BY W. R. ORNDORFF, R. C. GIBBS AND C. V. SHAPIRO[2]

RECEIVED JULY 30, 1927 PUBLISHED MARCH 7, 1928

The following investigation on the absorption of fluorescein was undertaken in the course of our study of triphenylmethane derivatives.[3] The absorption of fluorescein has been studied extensively in the past but the recorded data show wide variations. In the earlier work,[4] only solutions of alkali salts of fluorescein were employed. Meyer and Fischer[5] prepared a violet solution of fluorescein by boiling it with a concentrated solution of alkali. They called attention to the similarity of its absorption spectrum with that of phenolphthalein in dilute alkaline solution. Medhi and Watson[6] and Howe[7] compared the absorption of neutral and alkaline solutions of fluorescein in the visible and ultraviolet regions, respectively. Howe also reported on the absorption of fluoran in neutral and alkaline alcoholic solutions. Moir[8] studied the visible absorption of fluorescein in concd. sulfuric acid solution. Other reports on the absorption in the visible region were made by Nichols and Merritt,[9] Formánek and Knop[10] and Holmes.[11]

The lack of concordant results can be ascribed to two causes: (1) using impure materials, such as commercial preparations or extracts made directly from the fusion mixture; (2) neglecting to mention concentrations, both of fluorescein and alkali in the case of alkaline solutions, for

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[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled us to make the measurements described in this report is gratefully acknowledged.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1927.

[3] (a) Orndorff, Gibbs and McNulty, THIS JOURNAL, 47, 2767 (1925); (b) Orndorff Gibbs and Shapiro, *ibid.*, 48, 1327 (1926); (c) Orndorff, Gibbs and McNulty, *ibid.*, 48, 1994 (1926); (d) Omdorff, Gibbs, McNulty and Shapiro, *ibid.*, 49, 1541 (1927).

[4] (a) G. Kriiss, *Ber.*, 18, 1426 (1885); (b) Z. *physik. Chem.*, 2,312 (1888); (c) Vogel, *Wied. Ann.*, 43,449 (1891); (d) P. Kriiss, Z. *physik. Chem.*, 51,257 (1905); (e) Meyer and Marx, *Ber.*, 40,3603 (1907); (f) Stark and Meyer, *Physik.* Z., 8,248 (1907); (g) Meyer and Marx, *Ber.*, 41,2446 (1908); (h) Meyer and Fischer, *Ber.*, 44, 1944 (1911); (i) Massol and Faucon, *Bull. soc. chim.*, 13,217 (1913).

[5] Meyer and Fischer, *Ber.*, 46, 70 (1913).

[6] Medhi and Watson, J. *Chem. Soc.*, 107, 1579 (1915).

[7] Howe, *Phys. Rev.*, 8, 674 (1916).

[8] Moir, *Trans. Roy. Soc. So. Africa*, 7, 5 (1918).

[9] Nichols and Merritt, THIS JOURNAL, 36, 707 (1914).

[10] Formánek and Knop, Z. *anal. Chem.*, 56, 273 (1917).

[11] Holmes, THIS JOURNAL, 46, 2770 (1924).

not only is the transition from the neutral state to the alkaline state a gradual one but also, as has been found in this Laboratory, hydrolysis effects are very marked.

The fluorescein used in this investigation was an analytically pure sample prepared by Dr. A. J. Hemmer under the direction of the senior author. He has shown[12] definitely that fluorescein exists in only two physical modifications—red and yellow. Various attempts were made to determine spectroscopically whether these might be chemically distinct individuals, that is, the red form, quinoid, and the yellow, lactoid. However, the result of examining both forms in a number of solvents showed conclusively that they give identical absorption and that both exist in solution in the quinoid state. This last conclusion is based on the fact that compounds closely related to fluorescein but known definitely to possess the lactoid structure, such as fluoran, dichlorofluoran and fluorescein diacetate, show a characteristic absorption which is entirely different from that of fluorescein in neutral alcoholic solution. Again, fluorescein crystallizes from a pyridine solution in the form of bright yellow crystals, but a pyridine solution shows exactly the same type of absorption bands, up to its limit of transmission at about frequency number 3000, as a neutral alcohol solution, which deposits red crystals on concentration.

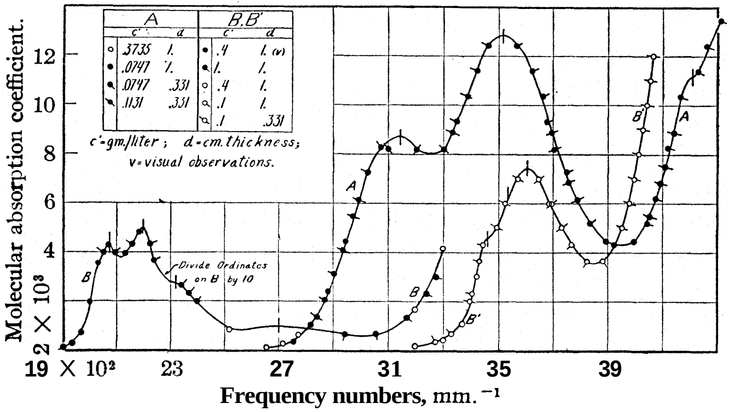

Fig. 1.—Neutral absolute alcohol solution: A, 2,4-dihydroxy-*o*-benzoylbenzoic acid; B,B′, fluorescein.

As crystals large enough to use for observing their absorption spectrum could not be obtained, some experiments were made on the selective reflection of the powdered red and yellow forms. The results, while indicating some differences between the two modifications of fluorescein, do not seem sufficiently decisive to warrant presentation here in detail.

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[12] Orndorff and Hemmer, This Journal, 49, 1272 (1927).

Fig. 1 shows the absorption in neutral absolute alcohol of fluorescein and of 2,4-dihydroxybenzoyl-*o*-benzoic acid, the intermediate product in the formation of fluorescein by the condensation of phthalic anhydride and resorcinol. 2,4-Dihydroxybenzoyl-*o*-benzoic acid, Curve A, has two bands at frequency numbers 3144 and 3515, and a shoulder at 4208. There is no apparent similarity to the absorption of fluorescein, despite the synthetic relation between the two compounds. However, the authors expect to make a further study of the intermediate acids, which are diphenylmethane derivatives, for the purpose of comparison with the corresponding phthaleins, which in turn are derivatives of triphenylmethane. The absorption spectrum of fluorescein, curve B,B′, shows two bands in the visible region at frequency numbers 2075 and 2198 and two bands in the near ultraviolet at 2319 and 2700. These four bands are similar in shape to the first four bands in resorcinolbenzein,[3b] although the intensity of these bands in fluorescein is only one-twentieth of that for the corresponding bands in resorcinolbenzein. In the further ultraviolet, fluorescein possesses bands at 3460, 3533 and 3604, but in this region there appears to be no close resemblance to resorcinolbenzein.

Some observations on the absorption of fluorescein in neutral aqueous solution were made, although no quantitative measurements on the absorption coefficient were attempted because of the extremely low solubility of fluorescein in water. A saturated solution, prepared by allowing ammonia-free distilled water to stand over finely divided fluorescein in a quartz[13] flask, showed two bands in the visible at 2090 and 2203, with several more in the ultraviolet which could not be accurately located because of the high transmissivity of the solution in this region. However, the general character of the absorption is entirely similar to that in alcoholic solution. In this respect fluorescein does not behave like some of the colored sulfonephthaleins,[14] which give different types of absorption in neutral alcohol and water solutions. It is a well known fact that, when these sulfonephthaleins are used as indicators, the color changes do not occur at the same values of P_H in alcoholic and aqueous solutions.

Fig. 2 shows the absorption of fluoran, 4,4′-dichlorofluoran and fluorescein diacetate in neutral alcoholic solution. The three substances show very similar absorption and, though they all contain the pyrone ring, there appears to be a very close resemblance to the absorption of diphenylphthalide, phenolphthalein (*p*,*p*′-dihydroxydiphenylphthalide) and isophenolphthalein (*o*,*p*′-dihydroxydiphenylphthalide).[3c] Since fluoran may be regarded as anhydro *o*,*o*′-dihydroxydiphenylphthalide, this

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[13] Glass vessels yield sufficient alkali to water on prolonged standing to bring out the fluorescence characteristic of alkaline solutions of fluorescein and to change the absorption markedly.

[14] Unpublished data

relation was to be expected. However, the introduction of hydroxyl groups meta to the pyrone oxygen (and apparently in the meta position only) radically changes the character of the absorption, as is shown by fluorescein in Fig. 1. Hydroquinolphthalein, in which the hydroxyl groups are para to the pyrone oxygen, is a colorless compound and its absorption[1]* in neutral solution is closely related to that of fluoran. The

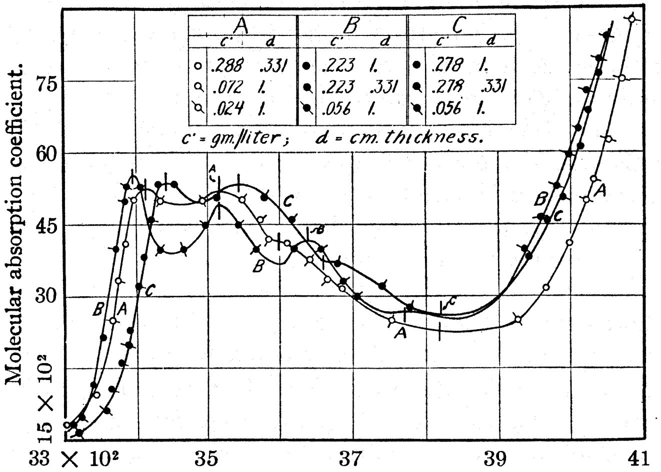

Fig. 2.—Neutral absolute alcohol solution: A, fluoran; B, 4,4'-dichloro fluoran; C, fluorescein diacetate.

frequency numbers of the absorption bands of fluorescein and the fluoran derivatives are given in Table I.

TABLE I

FREQUENCY NUMBERS OF BANDS IN NEUTRAL ALCOHOLIC SOLUTIONS

Fluorescein	Dihydroxy-benzoyl-o-benzoic acid	Fluoran	4,4'-Dichloro-fluoran	Fluorescein diacetate
2075	....	....	....	....
2198	....	...	....	....
2319	....	....	....	....
2700	....	....	....	....
3460	3144	3413	3394	3441
3533	3515	3517	3516	3544
3604	4208	3597	3638	3660
....	....	3818	3771	3820

When either the red or yellow forms of fluorescein are dissolved in 75% formic acid, only the yellow form is obtained on crystallization. The absorption of such a solution, Curve C, Fig. 3, is, however, entirely similar to the absorption of fluorescein in concentrated sulfuric acid, Curve B, Fig. 3. The conclusion to be drawn is that the fluorescein while in solution is present in both cases as the salt of the respective acids. The sulfate of fluorescein has been isolated from a 35% sulfuric acid solution by A. J. Hemmer.[15] Formic acid solutions on concentration, however, yield not the formate but fluorescein itself. The absorption of fluorescein in concd. sulfuric acid is characterized by a strong band at 2317 and a prominent double band in the ultraviolet at 3906 and 4005, with weaker bands at 3039, 3215 and 3541. It is entirely analogous to the absorption of resorcinolbenzein[3b] in concd. sulfuric acid. Fluoran dissolves in concd. sulfuric acid to form a yellow solution with a faint green fluorescence. In the visible region, Curve A, there are three weak bands at 2135, 2239 and 2343, while in the ultraviolet there is a prominent band

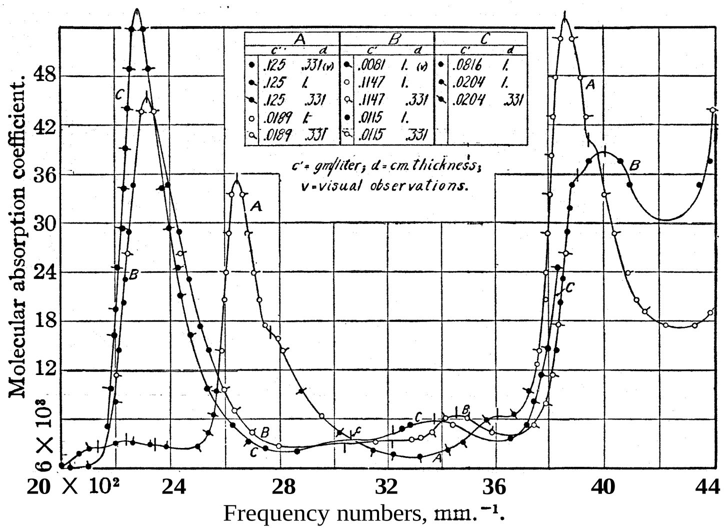

Fig. 3.—Concentrated (93%) sulfuric acid solution: A, fluoran; B, fluorescein. 75% formic acid solution: C, fluorescein.

at 2646 with a shoulder on its short wave length side at 2765 and in the further ultraviolet a shoulder at 3605, a very intense band at 3862 and a shoulder at 3945. It is possible to account for this difference in the absorption of fluoran and fluorescein in sulfuric acid solution by assuming that in the former the pyrone oxygen carries the basic properties while in the latter the quinoid oxygen has the greater basicity.

Fig. 4 shows the effect on the absorption of fluorescein due to the addition of various amounts of dry hydrogen chloride gas to the neutral alcoholic solution. With four molecules of hydrogen chloride to one of fluorescein, Curve A, there is an increase of absorption at frequency number 2254 while the band at 2085 has become much weaker, the remainder of the spectrum being still very similar to that of neutral fluorescein. In-

[15] Hemmer, *Dissertation*, Cornell University, 1926.

creasing the hydrogen chloride content to 155 molecules, Curve B, and to 960 molecules, Curve C, completely changes the character of the absorption, the bands for the latter solution being located at 2258, 3240, 3349, 3790 and 4018. The latter two bands appear to be approaching the type of double band found in the concd. sulfuric acid solution at 3906 and 4005, a behavior analogous to that of resorcinolbenzein under the same conditions, thus giving evidence of the presence of a hydrochloride of fluorescein, which has been isolated and analyzed by Gattermann.[16]

Fluorescein, when dissolved in alcoholic alkali, exhibits the phenomenon that we have previously termed reversion,[3b] an hydrolysis-like effect; that is, at low concentrations of alkali, dilution of the solution causes the absorption to revert from the characteristic alkaline type to the neutral type. To avoid this complication, we have chosen to measure the absorption of the alkaline solutions at constant concentrations of fluorescein, but at different thicknesses. In so far as possible, the concentrations were kept approximately the same for the various ratios of potassium hydroxide employed in order to follow better the progressive change in absorption with increase of alkali. In Fig. 5, Curve **A** for one molecule of potassium hydroxide to one of fluorescein shows the same bands as fluorescein in neutral solution except that the visible bands at 2075, 2199 and 2318 are more than ten times as intense. There is also a new band at 3174. In Curve B for three molecules of potassium hydroxide, and Curve C for twenty molecules, the absorption of the dipotassium salt of fluorescein is more clearly brought out, the latter curve showing bands

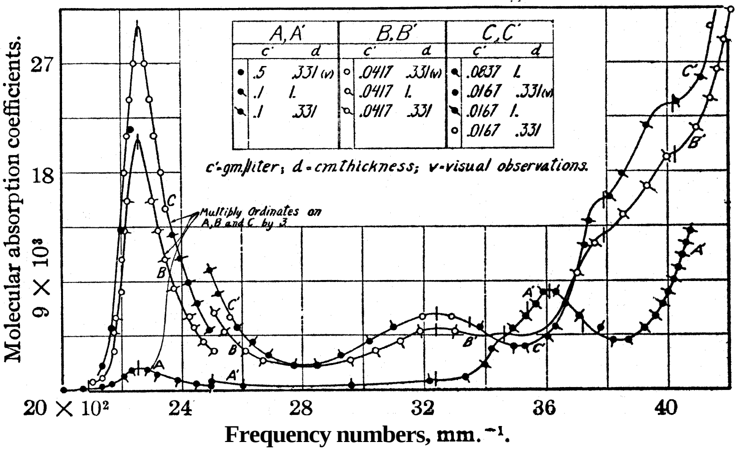

Fig. 4.—Fluorescein in alcoholic HCl solution: A,A′, 1 molecule: 4 molecules of HCl; B,B′, 1 molecule: 155 molecules of HCl; C,C′, 1 molecule: 960 molecules of HCl.

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[16] Gattermann, *Ber.*, 32, 1135 (1899).

at 2005, 2153, 2673, 3082, 3423, 3823 and 4138. Higher ratios of potassium hydroxide in alcohol show no further change in the absorption.

Fluorescein dissolves in cold 33% aqueous potassium hydroxide with a deep orange color and an intense green fluorescence. The absorption of the freshly prepared solution is given in Fig. 6, Curve A,A′. In the visible region there are two bands, a very weak one at 1715 and an extremely intense one at **2033,** while in the ultraviolet there are bands at **2628, 3088** and **3502.** With the exception of the first, these agree closely with the bands found in a solution of resorcinolbenzein[3b] in 5% aqueous potassium hydroxide. However, this strongly alkaline solution changes

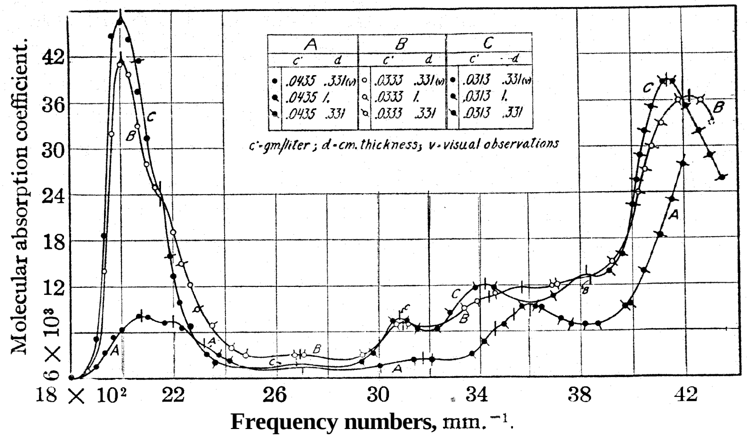


Fig. 5.—Fluorescein in alcoholic KOH solution: A, 1 molecule : 1 molecule of KOH; B, 1 molecule : 3 molecules of KOH; C, 1 molecule : 20 molecules of KOH.

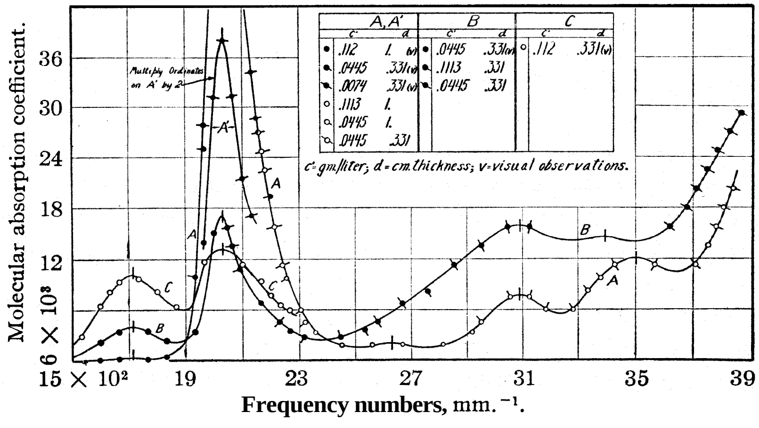
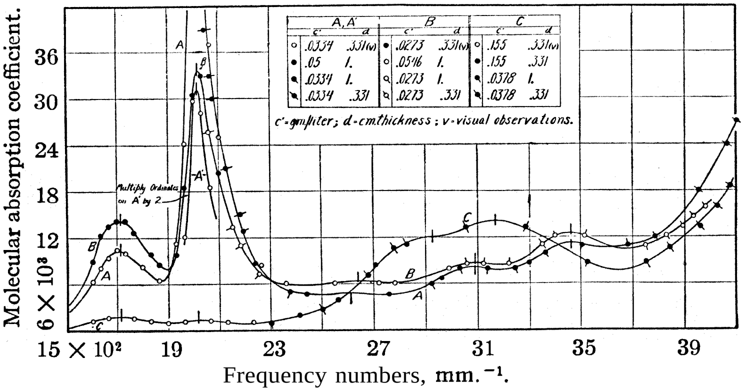


Fig. 6.—Fluorescein in cold 33% aqueous KOH: A,A′, fresh solution; B, solution A after standing for five weeks; C, solution A after standing for ten weeks.

over in a few weeks from an orange color to a deep purple and then gradually fades out over several months to a pale pink, even though kept in a dark room. Curve B shows an intermediate stage. A still later stage is shown in Curve C, the band at 1715 still growing and the one at 2033 still decreasing, which accounts for the observed change in color, from orange to purple. **Baeyer**[17] has called attention to a change of this kind when a solution of fluorescein in strong alkali is boiled and he has explained it by the rupture of the pyrone ring with the formation of a **tetra**basic salt. Meyer and **Fischer**[5] have measured the absorption of such a solution and claim to have found a resemblance to the absorption of phenolphthalein in weak alkaline solution. A comparison of the data here with our results on **phenolphthalein**[3c] gives no indication of any simple relation between the two compounds. As a further check on these results, the purple solution was prepared by dissolving fluorescein together with a weighed amount of potassium hydroxide in the required volume of water, the heat of solution of the potassium hydroxide being sufficient to produce the purple solution instantaneously.



Pig. 7.—Fluorescein in hot 33% aqueous KOH: A,A', fresh solution; **B.** solution A after standing for twelve hours; C, solution A after standing **for** seven weeks.

The absorption of this solution was measured as soon as it had cooled and it is shown in Fig. 7, Curve A,A'. The band at 1715 is quite intense, while that at 2018 is somewhat less intense than the corresponding one in the freshly prepared, cold solution of fluorescein. Twelve hours later the band at 1715 has increased by one-fourth and the one at 2018 has decreased about half, while the bands in the ultraviolet have all increased to some extent. At the end of six weeks, the solution had faded to a pale pink and the absorption, Curve C, shows the bands at 1715 and 2018 as very weak, while the ultraviolet absorption has changed in character,

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[17] **Baeyer,** Ann., 372, 108 (1909).

with two bands at 2926 and 3168. Neither Baeyer nor Meyer and Fischer have mentioned this progressive change in the color of the solution. There would thus appear to be two processes at work: (1) the rupture of the pyrone ring, represented by the growth of the band at 1715; (2) some other disruptive process preceded possibly by the formation of a carbinol, which causes both visible bands eventually to fade out, while producing a different type of absorption in the ultraviolet. The behavior of eosin and sulfonefluorescein is being studied under similar conditions.

In Table II the positions of the bands in the various acid and alkaline solutions of fluorescein are summarized.

TABLE II

FREQUENCY NUMBERS OF BANDS IN SOLUTIONS OF FLUORESCEIN

Neutral alcohol	Alcoholic HCl 4 m.	Alcoholic HCl 155 m.	Alcoholic HCl 960 m.	Concd. sulfuric acid	75% formic acid
2075	2085	..	..	..	..
2198	2254	2257	2258	2317	2285
2319	3236	3238	3240	3039	3062
2700	3462	3360	3349	3215	3219
3460	3536	..	..	3451	3372
3533	3609	..	..	..	
3604	3719	3790	3790	3906	
..	..	4024	4018	4005	

Neutral alcohol	Alcoholic KOH I m.	Alcoholic KOH 3 m.	Alcoholic KOH 20 m.	Aqueous 33% KOH Cold Fresh	Aqueous 33% KOH Cold Faded	Aqueous 33% KOH Hot Fresh	Aqueous 33% KOH Hot Faded
..		..	..	1715	1715	1715	1715
		2005	2005	2033	2033	2018	2018
2075	2075	..	..				
..	..	2151	2153				
2198	2199		..				
2319	2318	..	..	..	..	..	..
2700	2698	2688	2673	2628	..	2612	..
..	3174	3095	3082	3088	3090	3089	2926
3460	3460	3437	3423	..	3395	..	3168
3533	3535	3570		3502	..	3461	..
3604	3604	..					
		3840	3823				
		4225	4138				

Summary

1. The absorption curves of fluorescein, fluorescein diacetate, fluoran and dichlorofluoran in neutral alcoholic solutions have been determined. It has been concluded that fluorescein exists in solution in the quinoid state only.

2. The absorption curves of fluorescein in concd. sulfuric acid, 75% formic acid and in alcoholic solutions of hydrogen chloride indicate that the fluorescein is present in each case as the salt of the respective acid.

3. The effect of the addition of various amounts of potassium hydroxide to the alcoholic solution of fluorescein, due to the formation of the dipotassium salt of fluorescein, has been studied.

4. The absorption of fluorescein in strong aqueous potassium hydroxide undergoes a progressive change, indicating the occurrence of two processes: (1) the rupture of the pyrone ring and (2) the possible formation of a carbinol followed by some other disruptive process.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS[1]

GEORGE GLOCKLER[2] AND L. D. ROBERTS[3]

RECEIVED SEPTEMBER 26.1927 PUBLISHED MARCH 7, 1928

Many methods for the determination of oxygen in organic compounds have been described.[4] In all these methods it is necessary to perform a ***separate*** experiment for the determination of oxygen. In the new method proposed here we determine the amount of oxygen consumed ***during*** the combustion of an organic compound *gasometrically* and are thus able to analyze for Carbon, Hydrogen ***and*** Oxygen in ***one*** operation.

We used the modification of Wise's[5] semi-micro combustion method which has been developed and used in this laboratory by Dr. W. M. Lauer

Apparatus and Procedure

The apparatus used is shown in Fig. 1. Oxygen was made from solid potassium permanganate and measured (N. T. P.) in a Ramsay buret. The combustion tube contained platinized asbestos only. The use of copper oxide was avoided at this time following a suggestion of Professor W. H. Hunter. It is possible that copper oxide wire reduced to copper during the combustion may not be reoxidized to the same extent as it had been originally. The sample was weighed on an ordinary analytical balance, as were the absorption tubes.

[1] This method was devised in examining the liquid product obtained in the course of the investigation on "the effect of electrical discharge on gaseous hydrocarbons," listed as research project No. 8 of American Petroleum Institute Research. Financial assistance for this work has been received from a research fund of the American Petroleum Institute, donated by the Universal Oil Products Co. 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 Associate.

[3] Professor of Chemistry. Colorado School of Mines.

[4] Older work: "Analyse, etc., org. Verbind.," Hans Meyer, 3rd ed., Julius Springer, Berlin, 1916, p. 301; M. C. Boswell, THIS JOURNAL, 35, 284 (1913); 36, 127 (1914); R. Strebinger, *Z. anal. Chem.*, *58*, 97 (1919); H. Ter Meulen, *Rec. trav. chim.*, *41*, 509 (1922); 43, 899 (1924); *Chem. Weekblad*, 23, 348 (1926).

[5] Wise, THIS JOURNAL, 39, 2055 (1917).

At the beginning of an analysis the apparatus was brought to atmospheric pressure by opening stopcock A. Sample and absorption tubes were, of course, in place. The mercury in vessel B was placed on the mark C and stopcock D was closed. Room temperature and barometer were noted. Oxygen sufficient for the combustion was transferred to the vessel B so that all of it would take part in the flow through the combustion tube. The circulation was started by causing the Sprengel pump to operate. By a previous calibration we had determined the proper rate of dropping the mercury so as to produce the usual flow of oxygen through the combustion tube. We allowed forty-five minutes for complete combustion and fifteen minutes for further sweeping.

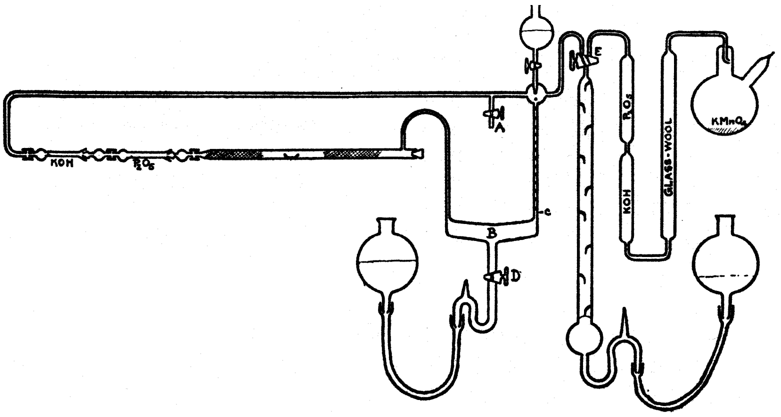

Fig. 1.

At the end of the experiment the apparatus was brought into its initial condition by removing the three pieces of triangular iron which comprised the furnace and all the hot asbestos shields and allowing room temperature to be attained. The remaining oxygen was now removed from vessel B, which was again filled with mercury to the mark C. Stopcock D was closed. The gas was thus transferred to the Ramsay buret, which was set to atmospheric pressure and stopcock E was closed. The oxygen remaining in the buret was measured and the absorption tubes were removed and weighed. An analysis can be carried out in two hours.

Blank experiments were run which showed some consumption of oxygen and gain of weight in the potassium hydroxide and pentoxide absorption tubes. However, oxygen thus treated and run through a second blank shows a negligible decrease in volume and the gains in the absorption tubes are also negligible. In further work we expect to pretreat the oxygen as it comes from the generator, thus avoiding the necessity of making blank experiments.

A very important feature of our apparatus is that the system is closed and any gases due to cracking or incomplete combustion (such as methane and carbon monoxide) are carried back through the hot combustion tube several times in the period allowed for the combustion. Thus our method tends to insure complete combustion.

Results

That the method yields good results can be seen from the data on benzoic acid[6] given in Table I. The calculation of the percentage of oxygen found by our method (Col. 5) is obvious and need not be given in detail.

TABLE I

DATA ON BENZOIC ACID

Sample taken, mg.	H, %	C. %	Oxygen, %		Total	100−Total
			By difference 100%−%H−%C	From O_2 consumption		
30.1	5.93	69.45	24.62	24.59	99.97	$0.03
34.5	5.51	67.92	26.57	26.04	99.49	+ .51
34.8	4.93	68.14	26.93	25.00	98.07	+1.93
33.65	5.12	69.30	25.58	26.45	100.87	−0.87
Average	5.37	68.70	25.93	25.53	99.60	+ .40
Calcd.	4.96	68.82	26.22	26.22	100.0	
	0.41	0.12	0.29	0.69	0.40	

That the method here proposed is of value was shown by combustions made on a volatile oil obtained from ethane under the influence of electrical discharge in an ozonizer.[7] Combustions were made of this oil by the ordinary semi-micro method which indicated that carbon and hydrogen together amount to only 87%. The individual experiments checked satisfactorily. Had the ordinary procedure of the organic chemist been adopted it would have been concluded that the oil contained 13% of oxygen. However, from its origin from ethane in a closed system this appeared improbable. By special experiments it was shown that it did not absorb oxygen rapidly. This perplexity led to the method of combustion described, by which it was immediately possible to show that the oil in question contained carbon and hydrogen only and no oxygen. In this case the failure of the ordinary method of combustion is evidently due to some form of incomplete combustion.

It is in cases like the one described above that the method will find its greatest use. One would naturally take the per cent. of oxygen as obtained by difference as the more accurate figure after having demonstrated by this method that oxygen actually is contained in a given compound.

[6] Bureau of Standards Sample.

[7] Paper (Preprint No. 6) presented by S. C. Lind and Geo. Glockler at the September 5, 1927, Meeting of the American Electrochemical Society held at Minneapolis, Minnesota.

We wish to thank Professor S. C. Lind for suggesting the method of attack and Professor W. H. Hunter for his interest in our work and helpful suggestions.

Summary

A new method is proposed which permits the determination of oxygen during the combustion of organic compounds containing carbon, hydrogen and oxygen. The amount of oxygen consumed is measured volumetrically. The arrangement of the combustion train in a closed circulating system insures complete combustion.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE BAKER CHEMICAL AND ROCKEFELLER PHYSICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF BENZENE AND TOLUENE IN ALCOHOLIC SOLUTION. THE SPECTROSCOPIC DETECTION OF BENZENE AS AN IMPURITY IN ORGANIC COMPOUNDS[1]

BY W. R. ORNDORFF, R. C. GIBBS, S. ALICE MCNULTY[2] AND C. V. SHAPIRO[3]

RECEIVED OCTOBER 13, 1927 PUBLISHED MARCH 7, 1928

Since Henri[4] succeeded in ordering the numerous lines in the absorption spectra of benzene vapor, in accordance with the modern view of band spectra, there has been a revival of interest in the absorption of the aromatic hydrocarbons. Henri and Walter[5] followed with a study of the vapor of toluene and Klingstedt[6] reported on its absorption spectrum in hexane solution. The latter was able to show that the relatively broad solution bands follow the same law that applies to the band heads in the vapor spectrum. Kronenberger and Pringsheim[7] have measured the absorption spectrum of solid benzene at −180°. They found that the diffuse bands of liquid benzene break up into many narrow bands of about 1 Å. in width, of which they record 62. These vary considerably in intensity, the most prominent being associated with the strong bands

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[1] The assistance of a grant made to the first two authors from the Heckscher Research Foundation of Cornell University which enabled us to make the measurements described in this report is gratefully acknowledged.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1921–1923 (now Mrs. H. F. Vieweg).

[3] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1927.

[4] Henri, *J. phys. radium*, **3**, 181 (1922). For a fairly complete bibliography of the early work on the absorption spectra of benzene and toluene, see "Report of the British Association for the Advancement of Science," 1916, p. 131.

[5] Henri and Walter, *Compt. rend.*, **176**, 746 (1923).

[6] Klingstedt, *ibid.*, **175**, 1065 (1922); *Acta Acad. Abo. Math. Phys.*, **3**, 1 (1924).

[7] Kronenberger and Pringsheim, *Z. Physik*, **40**, 75 (1926).

reported by Henri[4] for a pentane solution.[8] Kronenberger and Pringsheim call attention to the general similarity of the absorption of benzene at the low temperature and in the vapor state and attempt to arrange the bands on energy level diagrams, while pointing out the theoretical difficulties in the way of accepting any of the arrangements proposed. Despite the fact that the mechanism is obscure, the general equation deduced by Henri is still applicable, and with certain simplifications for the cases of solid and liquid (or dissolved) benzene, it expresses the data very satisfactorily. For the vapor spectra, the equation takes the form

$$\nu = \nu_0 + an - (bp + b'p^2) - \alpha(m^2 - q^2) \qquad (1)$$

where ν_0 is the frequency attributed to electronic vibrations, a and b correspond to intramolecular vibrational frequencies in the excited and unexcited states, b' is a correction introduced by the non-harmonic nature of the vibrations and α gives the molecular rotational frequency; n, p, m and q are quantum numbers. In the solid and liquid states, molecular rotation is absent, as evidenced by the lack of fine structure in the individual bands and the equation can be simplified to

$$\nu = \nu_0 + an - bp \qquad (2)$$

The factor in b' is neglected, since its value of 0.2 mm.^{-1} as determined from the vapor spectra of benzene is less than or, at best, of the same order of magnitude as the probable error in the location of band heads for solution spectra.

In a recent paper, Smith, Boord, Adams and Pease[9] have ascribed the ultraviolet bands in benzene vapor to the presence of the carbon-hydrogen linkage, on the basis of the numerical relationship with the infra-red bands of benzene. This accordance is achieved by neglecting the factor ν_0 and considering only the contributions to the energy of the molecule given by the vibrational factors a and b. However, a closer examination of the available data[10] shows that of the infra-red bands of benzene, some are characteristic of all compounds containing the CH_2 and CH_3 groups, others occur only in compounds containing the ethylenic bond, while still others are characteristic of benzene alone. This makes it appear very doubtful whether there is any justification for attributing the ultraviolet bands merely to the carbon-hydrogen linkage. The evidence adduced by Smith and his collaborators in support of their view indicated that a number of organic compounds of radically different types, such as cyclohexene, diethyl ether, methyl-n-amyl ether and ethylene chlorohydrin in the vapor state, all showed exactly the same bands, in position and

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[8] It would seem to be more appropriate to compare the bands in solid benzene with those in the liquid state, which Henri also measured, as this brings out more precisely the effect of change of state and decrease in temperature on the absorption

[9] Smith, Boord, **Adams** and Pease, THIS JOURNAL, 49, 1335 (1927).

[10] Henri, "Études de Photochimie," Paris, 1919, p. 113.

relative intensity, as benzene. The suspicion that these bands were actually due to the presence of benzene as an impurity has been confirmed by experiments carried out in this Laboratory, following in general the same procedure that was used by the above authors.[11]

The diethyl ether used was a sample of Kahlbaum's, distilled over sodium. The methyl-n-amyl ether, cyclohexene and ethylene chlorohydrin were obtained from the Eastman Kodak Company. These were first examined without any previous attempt at purification. The diethyl ether and cyclohexene showed no indication of benzene bands, while both the ethylene chlorohydrin and methyl-n-amyl ether gave the characteristic vapor bands very strongly. The latter two substances were then carefully distilled and again examined, with the result that the ethylene chlorohydrin now gave no trace of the benzene bands, while with the methyl-n-amyl ether no change in the intensity of the bands was apparent. Following a suggestion from Dr. H. T. Clarke of the Eastman Kodak Company, the ether was purified by dissolving in concd. sulfuric acid, blowing dry air through the cold solution for one hour, then diluting with ten volumes of water and distilling. The vapor from the sample so obtained was found to be perfectly transparent, with no trace of the characteristic bands of benzene.

The question of the possible source of benzene in the contaminated samples was also considered. In the case of ethylene chlorohydrin, we were informed that benzene was used as the dehydrating agent in the course of its purification, which satisfactorily accounts for the 0.06% found in the product. The presence of benzene in methyl-*n*-amyl ether may be explained either by the fact that the commercial diethyl ether used in its preparation by the Grignard reaction might have been contaminated by benzene or that the methyl-n-amyl ether might have absorbed benzene vapor from the atmosphere of the laboratory during its preparation. Commercial ether has, at times, been manufactured from alcohol denatured with benzene, although a sample of technical ether from current production at the U. S. Industrial Alcohol Co. showed no indication of benzene as an impurity. The second suggestion appears, therefore, to be the more probable, especially as it was found that when a sample of some pure non-volatile organic liquid, such as ethylene chlorohydrin, was allowed to stand in an open container near an open vessel of benzene for ten hours its absorption spectrum revealed the presence of appreciable traces of benzene.

As the form of vapor apparatus used in the above experiments does not permit of quantitative determination of the benzene content of the

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[11] Since obtaining our data, de Laszlo, THIS JOURNAL, 49, 2106 (1927), has shown experimentally that ethylene chlorohydrin, when carefully purified, exhibits no trace of benzene bands.

samples, an examination of the liquids was undertaken with the Hilger sector photometer, following the method previously described.[12] It was found that both methyl-n-amyl ether and ethylene chlorohydrin contained sufficient benzene to give the characteristic solution bands of that substance. The following procedure was developed for its quantitative determination in the ethylene chlorohydrin. A series of exposures was made at different sector openings, using the original, contaminated sample in the solution cell and the twice redistilled material in the solvent cell. From the plate an approximate determination of the benzene concentration could be obtained by reference to the absorption curve for the alcoholic solution (see below). A solution of equivalent concentration was then prepared by dissolving a weighed amount of benzene in a given volume of pure ethylene chlorohydrin, The absorption of this solution was determined in the usual manner against pure ethylene chlorohydrin as standard and from the curve so obtained it was at once possible to calculate the concentration of benzene in the contaminated sample. To carry out the calculation, a curve is drawn for the known solution, plotting absorption coefficient against frequency numbers, the absorption coefficient being defined by the relation

$$\beta = \frac{m}{cd} \log \frac{1}{T}$$

where m = molecular weight, c = concentration in g./liter, d = thickness of cell and $1/T$ = reciprocal of the transmittance. For the unknown solution, a series of exposures is made for different values of log $1/T$ and the corresponding values of the frequency numbers are determined from the plate. From the curve for the known solution, the values of β corresponding to these frequency numbers are read off and, by substituting in the above expression, c can be calculated. The sample of ethylene chlorohydrin, as received, contained 0.06% of benzene, while it was estimated by a somewhat cruder method that the methyl-n-amyl ether contained about 0.7–0.8% of benzene.

In determining the absorption spectra of benzene and toluene in alcoholic solution, special precautions were taken, because of their high volatility and the intense absorption of their vapors, to exclude them from the atmosphere of the laboratory and particularly to prevent local concentration between the light source and the slit of the spectrograph. The ends of the cell tubes for holding the solutions were carefully ground to prevent leakage and were filled completely, thus avoiding the presence of small bubbles which would be saturated with active vapor. As a final check, photographs of the absorption spectra of the vapors of benzene and toluene were made and compared with those of the solutions. A study of the relative positions and character of the vapor and solution

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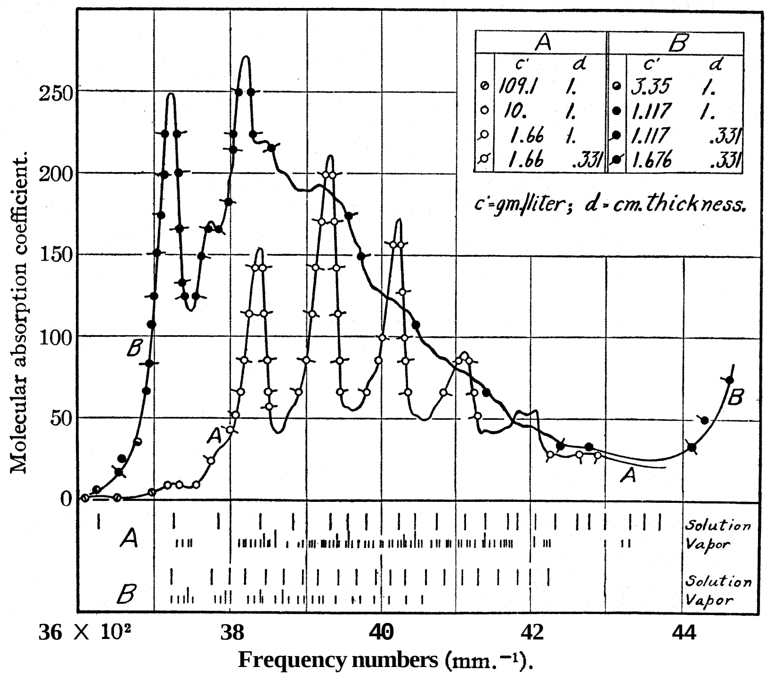
[12] Orndorff, Gibbs and McNulty, THIS JOURNAL, 47, 2767 (1925).

bands showed conclusively that none of the absorption bands found in solution could be ascribed to vapor. Two samples of benzene were examined, the first being redistilled from Kahlbaum's thiophene-free product, the other prepared from pure benzoic acid and redistilled. Both samples had a boiling point of 79° at 739.5 mm. They gave entirely concordant results. The toluene used was redistilled from a pure Kahlbaum sample. Its boiling point was 108.8° at 743 mm.

The absorption curves for absolute ethyl alcohol solutions of benzene and toluene are sketched in Fig. 1. The positions of the bands have been indicated on the same diagram, together with our measurements on the vapor spectra. Our apparatus was quite unsuited for bringing out the already well-known finer structure of these vapor bands, but they are included here primarily as evidence of the lack of consistent coincidence with the fainter solution bands. It will be noted that between frequency numbers 3600 and 4400 there are 23 solution bands for benzene and 21 for toluene, as against 8 tabulated by Henri[13] for benzene and 16 listed by Klingstedt[6] for toluene in hexane solution. Henri recorded but 7



A, Benzene; B, Toluene.

Fig. 1.—Neutral absolute alcohol solution.

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[13] Henri's curve indicates the presence of six more weak bands, whose positions he did not tabulate in frequency numbers.

bands for an alcoholic solution of benzene, his values being in very close agreement with ours. As pointed out by Henri, there is an average displacement of 5 mm.$^{-1}$ toward higher frequency numbers for the bands in an alcoholic solution of benzene as compared with their position in a hexane solution. Comparing Klingstedt's data with ours, the same average shift is found in the corresponding case for toluene. As shown in Fig. 1, the intensity of absorption is, on the whole, greater for toluene than for benzene in alcoholic solution. For hexane solutions, however, Klingstedt's curves show benzene to have a greater intensity, and toluene a lesser intensity, than our data show for the corresponding alcoholic solutions.

The frequency numbers (mm.$^{-1}$) of the absorption bands of benzene and toluene are arranged in Table I according to equation (2).

TABLE I

DATA FOR BENZENE AND TOLUENE

Frequency Numbers (mm.$^{-1}$) of Bands

Benzene				Toluene			
3628 **(98)**	..	..	..				
3726 **(114)**	..	..	..	3723 **(97)**	..	..	..
3840 **(92)**	..	..	..	3820 **(95)**	..	..	..
3932 **(92)**	..	3785 **(98)**	..	3915 (68) **(97)**	3847 (71) **(96)**	3776 **(95)**	..
4024 (69) **(89)**	3955 (72) **(91)**	3883 **(98)**	..	4012 (69) **(97)**	3943 (72) **(90)**	3871 (71) **(96)**	3800 **(96)**
4113 (67) **(95)**	4046 (65) **(94)**	3981 **(94)**	..	4109 (76) **(91)**	4033 (66) **(97)**	3967 (71) **(94)**	3896 **(97)**
4208 (68) **(92)**	4140 (65) **(95)**	4075 **(95)**	..	4200 (70)	4130 (69) **(96)**	4061 (68) **(96)**	3993 **(92)**
4300 (65)	4235 (65) **(97)**	4170 **(94)**	..	..	4226 (69)	4157 (72)	4085 **(98)**
..	4332 (68)	4264 (81) **(87)**	4183 **(96)**	..	..		4183
..	..	4351 (72)	4279 **(92)**				
..	..	..	4371				

Attention may be called to one point raised by Kronenberger and Pringsheim[7] regarding the separation of the bands in benzene. It will be noted that there is an average separation of 94 mm.$^{-1}$, with a single exception where the deviation is too large to be overlooked, the bands at 3726 and 3840 being separated by 114 mm.$^{-1}$. As the band corresponding to that at 3726 is the first one recorded by them; they have assumed that, if any bands of lower frequency numbers existed, they would be characterized also by this exceptional separation value. Our plates reveal, however, a band with relatively low intensity, at frequency number 3628, yielding a separation of 98 mm.$^{-1}$. As this band is sharply defined and easily measured, there is no doubt as to its exact location. It is possible that by using greater thicknesses of solid benzene at the low temperature this band might be observed and its position checked under those conditions. The data for toluene, when tabulated in a similar manner, show an average separation of 95 mm.$^{-1}$, which compares favorably with that of 94.3 mm.$^{-1}$, found by Klingstedt for a hexane solution.

Since the above article was submitted for publication, a correction by Smith, Boord, Adams and Pease to their previous article[9] has appeared in THIS JOURNAL, **49, 3137 (1927).**

Summary

1. The absorption curves of benzene and toluene in absolute ethyl alcohol solution have been determined and their relations discussed.

2. An analysis of their spectra shows that with one possible exception all of the observed bands of benzene and toluene can be arranged in series, in accordance with a simple mathematical expression.

3. The results recently reported by Smith, Boord, Adams and Pease indicating a benzene-like structure for the absorption spectra of diethyl ether, methyl-n-amyl ether, cyclohexene and ethylene chlorohydrin have been proved to be due to the presence of benzene as an impurity in these compounds.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE REACTIVITY OF THE METHYLATED SUGARS. II. THE ACTION OF DILUTE ALKALI ON TETRAMETHYL GLUCOSE

BY M. L. WOLFROM[1] WITH W. LEE LEWIS

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The conversion of one sugar into another and the chemistry of sugars in alkaline media are matters of interest to the biologist and pathologist, as well as the chemist. The course of these transformations can never be fixed with exactness until the underlying fundamental chemistry has been elucidated. The interconversion of simple sugars by alkali has been explained by assuming intermediate enol formation, but no direct proof of this has been obtained. Thus, the reciprocal interconversion of *d*-glucose, d-mannose and d-fructose, discovered by Lobry de Bruyn and

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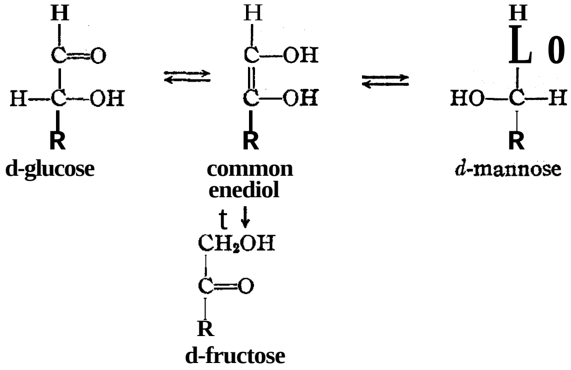
[1] **Abstracted from a dissertation submitted by M. L. Wolfrom to the Graduate** School **of Northwestern University, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.**

van Ekenstein,[2] is explained[3] by assuming an enediol common to the three sugars.



Sugar enol formation and interconversion were explained by Nef[4] on the basis of selective hydration and dehydration. This has been shown[5] to be incompatible with the behavior of the methylated sugars, as they would thus form hemi-acetals which would probably lose methyl alcohol almost as readily as the hypothetical hydrates of the non-methylated sugars would lose water. The experimental facts may be harmonized by replacing this conception of selective hydration and dehydration by a simple assumption of keto-enol tautomerism, due solely to the migration of a hydrogen atom.

The changes depicted in the formulas above represent the first steps in the action of dilute alkali on d-glucose. By increasing the time, temperature and concentration of alkali, more deep-seated changes take place. Enolization may progress down the carbon chain with the formation of other ketoses. That many of these more deep-seated changes occurred in the experimental work of Lobry de Bruyn and van Ekenstein and greatly complicated their results is evident from their own statements[6]

If the previously described common enediol explanation of the mutual interconversion of d-glucose, d-mannose and d-fructose is correct, then on applying this to the case of tetramethyl glucose, certain predictions may at once be made. In this derivative one of the labile hydrogen atoms is replaced by a stable methyl group and, consequently, only the 1,2-monomethyl enediol can form. This could not undergo all the changes possible for the unsubstituted enediol, since the methyl group of the methoxyl could not migrate in the same way, presumably, as the hydrogen of an hydroxyl. Thus the possible changes are as follows.

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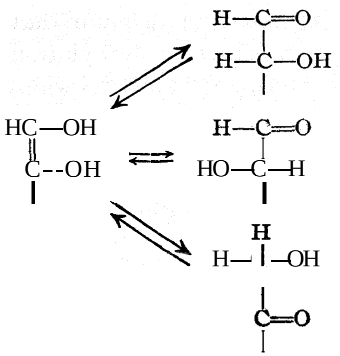
[2] Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, **14**, 195–207 (1895).

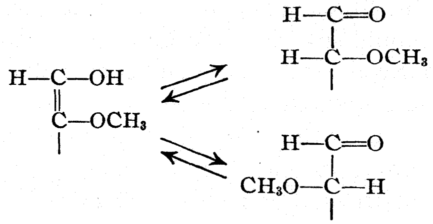
[3] Wohl and Neuberg, *Ber.*, 33, 3099 (1900).

[4] *(a)* Nef, *Ann.*, 357, 295 (1907); (b) Spoehr, *Am. Chem. J.*, 43, 228 (1910).

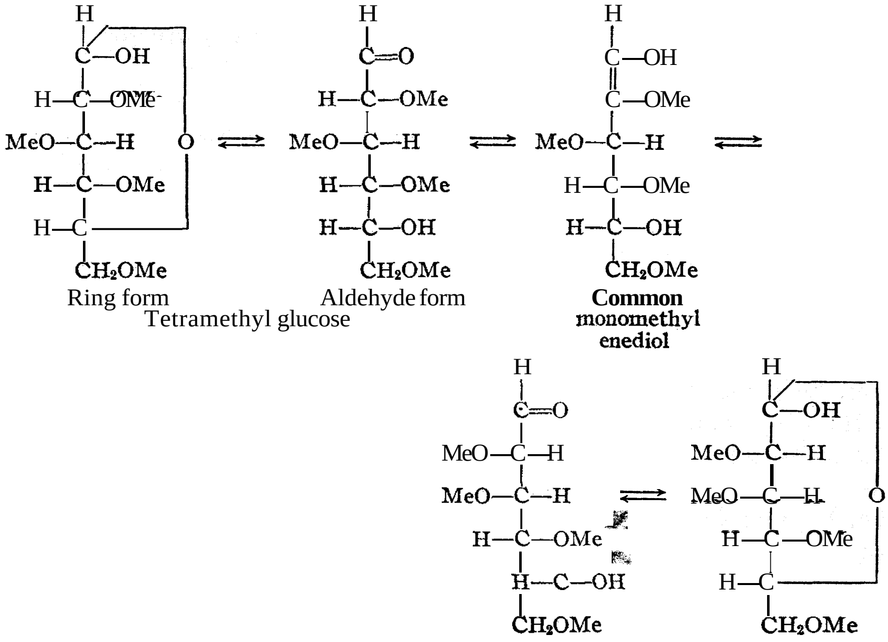
[5] Gustus and Lewis, This Journal, 49, 1513 (1927).

[6] Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, **15**, 93 (1896).





On the basis of these assumptions it would be expected that tetramethyl glucose would be converted by alkali into tetramethyl mannose but not into a methylated fructose. These changes may be formulated as follows.



Ring form Aldehyde form
Tetramethyl glucose

Common monomethyl enediol

Aldehyde form Ring form
Tetramethyl mannose

The existence of the aldehyde form of tetramethyl glucose has been proved by Levene and Meyer[7] through isolation of the open chain pentamethyl glucose. In the above formulas we have depicted tetramethyl glucose with the 1,5 oxidic ring in accordance with the most generally accepted evidence, although in our work we are not concerned with the absolute ether linkage.

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[7] Levene and Meyer, J. *Biol. Chem.*, **69**, 175 (1926).

In the unmethylated sugars interconvertibility does not demand that the final sugar have the same oxidic ring as its source. Methylation should fix the position of the oxidic ring so that two tetramethyl aldohexoses which are interconvertible should possess the same oxidic ring, whatever that may be.

In testing the deductions of the common enediol theory developed above, it was found necessary to establish first better interconversion conditions for d-glucose than are recorded in the literature. In the work of Lobry de Bruyn and van Ekenstein simultaneous saccharinic acid formation to the extent of 20 to 30% of the sugar used is recorded.[8] In this work saccharinic acid formation and the formation of ketoses other than fructose were finally restricted to a negligible amount by using extremely mild conditions. d-Glucose was converted by dilute alkali into a mixture of d-glucose, d-fructose and *d*-mannose. The amount of each sugar present was determined and it was found that under the conditions used, **31%** of the original glucose was changed to fructose, 2.5% to mannose, while **63.5%** remained unchanged.

The interconversion conditions established for glucose were then applied to tetramethyl glucose. On treatment of the equilibrated solution from tetramethyl glucose with acid it was proved by iodimetric methods that all of the original sugar was present as tetramethyl aldohexose, no ketose being present. The specific rotation of the resultant sugar mixture, 4–42 to +43°, was that required for an equal mixture of tetramethyl glucose, $[\alpha]_D = +82°$, and tetramethyl mannose, $[\alpha]_D = +2.4°$. The tetramethyl mannose used in this work was crystalline material.[9] The same constant specific rotation was reached on treating tetramethyl mannose[10] under the same conditions and a synthetic mixture of equal parts of tetramethyl glucose' and tetramethyl mannose maintained a stable rotation when treated with alkali. Solutions of tetramethyl glucose on treatment with different concentrations of dilute alkali showed widely differing initial polarimetric readings but all reached the value for the equimolecular mixture, the relatively large amount of tetramethyl mannose formed from tetramethyl glucose contrasting sharply with the behavior of the unmethylated glucose.

This sirupy mixture gave a high yield of crystalline anilide,[11] which together with the other analytical data indicates the presence of only negligible quantities of substances, other than the two epimers. Acids and methyl alcohol are not formed. The free sugars were recovered.

The abnormally high iodine value of the mixture dropped on acidifi-

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Ref. 2, pp. 198–199.

[9] Lewis and Greene, *Science*, 64,206 (1926).

[10] Unpublished work of R. D. Greene of this Laboratory.

[11] (a) Irvine, J. *Chem. Soc.*, 93, 103 (1908); (b) Irvine and McNicoll, *ibid.*, 97, 1452 (1910).

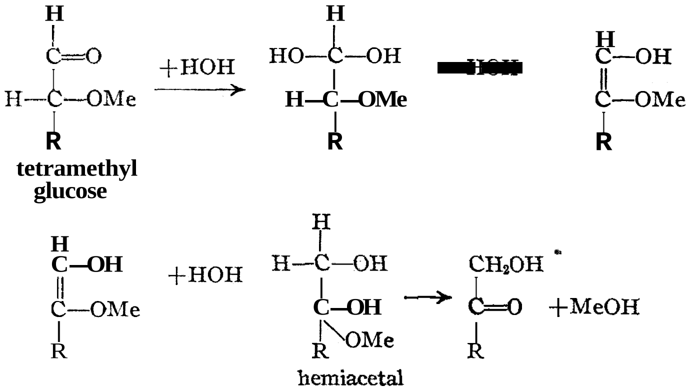
cation to the normal figure for a tetramethyl aldohexose solution, thus indicating the existence of a stable monomethyl enediol capable of consuming considerably more iodine.[12] Increasing the acid content did not alter the value.

These results were not shown by the unmethylated sugars, probably due to the decrease in stability of the enediols,[10] a point which is to be further investigated.

The experimental results obtained thus confirm the theory of a common enediol transformation in alkaline solvents, this in presence of acid yielding equal quantities of methylated glucose and mannose.

The bearing of this on the important controversial question of ring structure[13] of carbohydrates is also of particular interest. We have found that the so-called "normal" forms of tetramethyl glucose and tetramethyl mannose, prepared by methylation of the naturally occurring sugars, are mutually interconvertible and must, therefore, possess the *same* oxidic ring structure.[14]

From the experimental work some conclusions may also be drawn concerning the mechanism of keto-enol tautomerism in general. If, as is sometimes assumed, enol formation takes place through selective hydration and dehydration, then in the case of tetramethyl glucose hemiacetals would be formed. These, as previously noted, would readily lose methyl alcohol with the formation of partially methylated ketoses.



In this work no ketones and no methyl alcohol were found and, consequently, the selective hydration and dehydration theory of enediol formation is untenable at least in this instance. On the basis of our organic

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[12] Wislicenus and Thoma, Ann., 436, 43, 45 (1924).

[13] (a) Hudson, THIS JOURNAL, 48, 1424 (1926); (b) Levene and Sims, J. *Biol. Chem.*, 68, 737 (1926); (c) Charlton, Haworth and Peat, J. *Chem. Soc.*, 128, 82 (1926); (d) Hirst, ibid., 128, 350 (1926).

[14] *See,* however, Dale, THIS JOURNAL, 46, 1046 (1924); Hudson, *ibid.*, 48, 1433 (1926).

structural formulas the change is represented by a shift in the attachment of hydrogen between a carbon and oxygen atom, the mechanism of this shift not being one of chemical hydration and dehydration. It is conceivable that this deduction may be extended to the general theory of keto-enol tautomerism.

Experimental Part

Conversion of Glucose into Mannose and Fructose with Minimum Secondary Changes.—A molar solution of d-glucose in clear lime water saturated at 35° attained polarimetric equilibrium on standing for ten days at that temperature. Xylene was used as antiseptic agent. The initial acidimetric normality of the sugar solution was 0.035. The initial PH of the lime water alone was 12.6, which dropped to 10.6 on addition of the sugar. The solution very slowly changed to neutral and on standing for over a year had not developed any free acidity. The polarimetric changes are given in the following table and are plotted in Fig. 1.

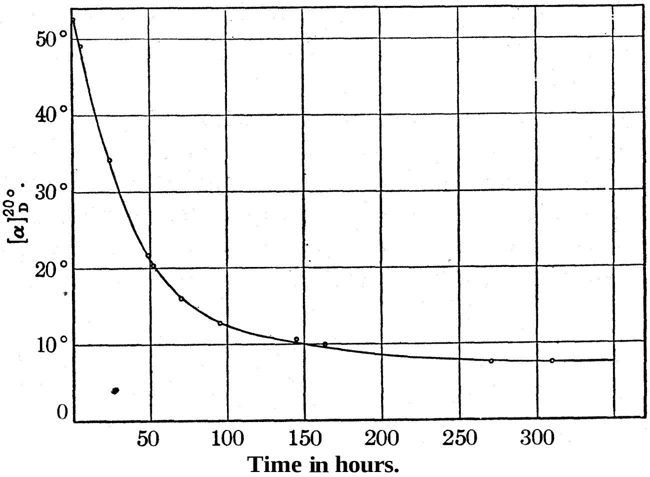

Fig. 1.—Polarimetric change of d-glucose in dilute alkali.

TABLE I

POLARIMETRIC CHANGE OF d-GLUCOSE IN DILUTE ALKALI

Time, hours	a, 20°, 2 dcm. tube, molar soln.	$[\alpha]^{20°}_D$	Time, hours	α, 20°, 2 dcm tube, molar soln.	$[\alpha]^{20°}_D$
0.5	+18.85°	+52.3°	94	4.61"	12.8"
1	18.80"	52.2"	144	3.88"	10.8°
5.5	17.78°	49.3"	163	3.54°	9.8"
23	12.31"	34.2"	270	2.7°	7.5"
48.5	7.78"	21.6"	310	2.7°	7.5"
53	7.36°	20.4"	25 days	2.7"	7.5"
70	5.81'	16.1'			

The equilibrated mixture was analyzed. The total reducing sugar content was determined by the Munson-Walker method[15] and corrected for the reducing power of the sugars concerned. The aldohexose content was determined by iodine oxidation according to the method of Cajori[16] modified for the presence of mannose by lengthening the time of oxidation to one hour. In both of these analyses suitable samples of the solutions were obtained by means of a weight pipet. The amount of mannose present was found, after concentration of the neutral solution to half volume, by quantitative precipitation as the phenylhydrazone under conditions precluding glucosazone formation, *viz.*, 5°.[17] These methods were checked in this Laboratory[10] with solutions of glucose, mannose and fructose of known composition and found to be accurate. The data determined follow.

TABLE II

ANALYSIS OF SUGAR SOLUTION FROM *d*-GLUCOSE

Original sugar content	16.83% by wt. soln.
Final reducing sugar content (calculated as glucose)	15.9%
Aldohexose content	11.07%
Mannose content	0.40%

The final analysis of transformed glucose calculated from the preceding data is given in Table III.

TABLE III

COMPOSITION OF SUGAR MIXTURE FROM d-GLUCOSE

Glucose	63.4%	Fructose	30.9%
Mannose	2.4%	Non-sugar substanees, probably saccharinic acids	3.3%

The final polarimetric reading calculated from the sugars in Table III would be +5, whereas +2.7 was the observed value.

These data show that no appreciable amount of ketoses other than fructose could be present as it is known that mixtures of these unfermentable ketoses have very low reducing properties (about half that of glucose) and slight optical activity.[18]

The rate of formation of fructose may be calculated with a fair degree of accuracy from the optical data since the change in rotation is indicative of the transformation of glucose into fructose. These data are plotted in Fig. 2 and are tabulated below.

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[15] Munson and Walker, THIS JOURNAL, 28,663 (1906).

[16] Cajori, J. *Biol. Chem.*, 54, 617 (1922).

[17] Sherrard and Blanco, *Ind. Eng. Chem.*, 15,612 (1923).

[18] (a) Lobry de Bruyn and van Ekenstein, *Rec. trav. chim.*, *16,* 256–263 (1897); (b) Dakin and Dudley, J. *Biol. Chem.*, 15, 127 (1913); (c) Spoehr and Wilbur, *ibid.*, 69,421 (1926).

TABLE IV

RATE OF TRANSFORMATION OF GLUCOSE INTO FRUCTOSE

Time, hours	Specific rotation	Original glucose converted into fructose, %
5.5	+49.3°	2.0
23	34.2	12.5
48.5	21.6	21.2
53	20.4	22.0
70	16.1	25.0
94	12.8	27.3
144	10.8	28.7
Final	7.5	31.0

Final value determined by analysis, + 30.9%.

Preparation of Methylated Sugars Used.—Four hundred and fifty g. of pure, twice recrystallized tetramethyl glucose, normal form (m. p. 88°; $[\alpha]_D^{20} = +82°$, c = molar) was prepared according to the method of W. N. **Haworth**,[19] suitably modified for the handling of large quantities of material. Four and four-tenths g. of tetramethyl fructose, normal form (m. p. 92–93°), was prepared in pure condition according to the method of Irvine and of Hudson.[20] Thii-six g. of tetramethyl mannose, normal form, was prepared according to the method of W. N. Haworth.[21] The sirup obtained by this method crystallized on nucleation with crystalline material obtained by R. D. Greene of this Laboratory[9] and was purified by recrystallization from low-boiling petroleum ether, m. p. 50–51°; $[\alpha]_D^{20} = +27.5°$ in methyl alcohol, c = 5.000.

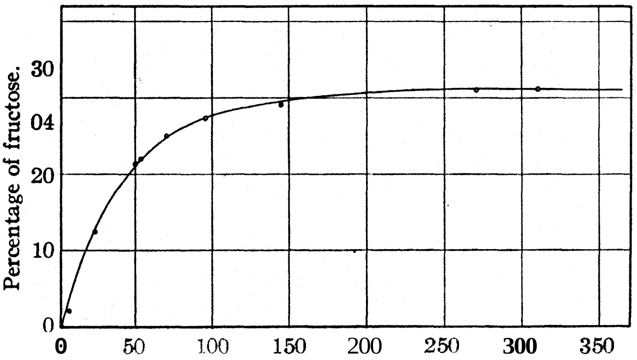

Fig. 2.—Transformation of glucose into fructose.

Application of Established Interconversion Conditions to Tetramethyl Glucose.—A molar solution of tetramethyl glucose in 0.035 normal calcium hydroxide solution changed in specific rotation from +82° to 42° (constant) on standing at 35° for 150 hours. The solution gradually became neutral and showed no acid reaction after standing at room temperature for several months. The equilibrated mixture was examined, as reported below, for the presence of ketoses, methyl alcohol and acids,

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[19] Haworth, J. *Chem. Soc.*, 107, 8 (1915).

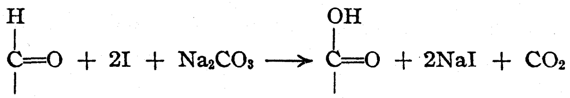
[20] (a) Irvine and Patterson, *ibid.*, 121, 2696 (1922); (b) Hudson and Brauns, THIS JOURNAL, 38, 1216 (1916).

[21] Ref. 19, p. 13.

after which its composition was established by optical data, and by separation of its components as anilides.

Proof of Absence of Ketoses in Equilibrated Mixtures from Tetramethyl Glucose.—Iodimetry is applied to the unmethylated hexose sugars to determine aldohexoses and thus ketohexoses by difference. Proper conditions were found in our work for the application of this method to the methylated sugars concerned. Attempts to use copper reducing values for determining tetramethyl aldohexose sugars were unsuccessful as the accuracy of the methods when applied to the methylated sugars is inadequate. The procedure adopted for the determination of methylated aldohexoses by iodimetry follows.

To 20 cc. of solution containing approximately 0.1 g. of methylated sugar in a glass stoppered flask, was pipetted 25 cc. of 0.1 N iodine solution. Four cc. of 2.75 normal sodium carbonate solution was then added. The mixture was allowed to stand for two to three hours at room temperature and in the dark. The sodium carbonate was then neutralized with 10% sulfuric acid and about 1.5 cc. of acid added in excess. The iodine remaining was titrated with 0.05 *N* sodium thiosulfate solution and the amount of iodine consumed calculated. With molar sugar solutions the sample was obtained by weighing the appropriate amount (0.5 cc.) of solution of determined density. Addition of iodine to the diluted sugar solution is essential as is also the order of addition of the iodine and carbonate. Under these conditions the theoretical amount of iodine was consumed according to the following equation.



$$\underset{|}{\overset{\overset{\displaystyle H}{|}}{C}}{=}O + 2I + Na_2CO_3 \longrightarrow \underset{|}{\overset{\overset{\displaystyle OH}{|}}{C}}{=}O + 2NaI + CO_2$$

Careful control work showed that neither the sodium carbonate nor the small amount of alkali introduced from the sugar solution interfered with the procedure. Variation in the room temperature (17 to 24°) also had no detectable effect. Oxidation was complete in two hours although another hour did not alter the figure beyond the limit of error. The oxidation of tetramethyl mannose was not complete at one hour. The data of Table V show that tetramethyl fructose is not oxidized under the conditions of the experiment.

TABLE V

STABILITY OF TETRAMETHYL FRUCTOSE TOWARD IODINE OXIDATION

	a	b
Tetramethyl fructose, g.	0.1000	0.1000
Iodine added, cc.	25.00	25.00
Iodine unused, cc.	24.95	24.95

The data of Table VI show that the procedure is applicable to mixtures of the two aldoses and in mixtures of the three sugars gives accurate results for tetramethyl fructose when the total sugar content is known.

Application of Established Iodimetric Method to Equilibrated Solution.—Application of this method to the equilibrated solution from tetramethyl glucose gave a value of 135–140% tetramethyl aldohexose. This was at first thought to be due to the reactive "gamma" form of tetramethyl mannose, but this form was not present, as the resulting

TABLE VI

IODIMETRIC ANALYSIS OF KNOWN MIXTURES OF METHYLATED SUGARS

Anal.		Tetramethyl glucose g.	%	Tetramethyl mannose g.	%	Tetramethyl aldohexose g.	%	Tetramethyl fructose g.	%
No. 1	Known	0.0581	57.8	0.0425	42 2	0.1006	100.0	....	. .
	Found	....	..	....	..	.0991	98.7		
No. 2		.0585	59.1	.0405	40.9	.0990	100.0		
	Found	....	..	....	..	.1002	101.0		
No. 3	Known	.0609	60.4	.0399	39.6	.1008	100.0		
	Found	....	..	....	..	.1005	99.7		
	Known	.0593	58.5	.0420	41.5	.1013	100.0	. . .	
	Found	....	..	....	..	.1016	100.4	....	. .
	Known	.0500	45.2	.0210	18.9	.0710	64.2	0.0396	35.8
	Found			....	..	.0706	63.8	. . .	36.2"
	Known	0500	45.2	.0210	18.9	.0710	64.2	.0396	35 8
	{Found		..	. .	.	.0709	64.1		35.9'

[a] By difference.

sirup did not condense[22] rapidly at room temperature with absolute methyl alcohol containing 0.25% of dry hydrogen chloride. The abnormal result could be accounted for if a relatively stable form of the common monomethyl-enediol was present since, due to its ethylenic nature, it would absorb halogen. If this were true, treatment with acid should revert the enol to the more stable keto form and the iodine value should be lowered. This was found to be the case and on increasing the acidification or "de-enolizing" conditions the constant value of 100% tetramethyl aldohexose was obtained.

TABLE VII

EQUILIBRATED MIXTURE PROM TETRAMETHYL GLUCOSE. CONSTANCY OP 100% APPARENT ALDOHEXOSE IODINE VALUE

Normality HCI	Time, standing, hours	Temp., °C.	Apparent tetramethyl aldohexose, % Reaction mixture	Control[a]
	..	..	137	...
1	0.5	20	113	...
1	24	20	105	99.4
2	36	35	100	100
3	54	35	99.4	100

Concentration of sugar in acid soln. = 0.5%.

[a] Pure methylated sugar solns. of known compositions.

For these acid solutions the iodimetric procedure was modified as follows.

The iodine was added to the acid solution and the acid then neutralized by dropwise addition of the previously determined amount of standard sodium hydroxide solution. The customary amount of sodium carbonate was then added and the solution allowed to stand, etc. Carbonate

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[22] Irvine and Burt, J. *Chem. Soc.*, 125, 1347 (1924).

neutralization cannot be used as the carbon dioxide formed renders the resulting oxidation mixture too acid.

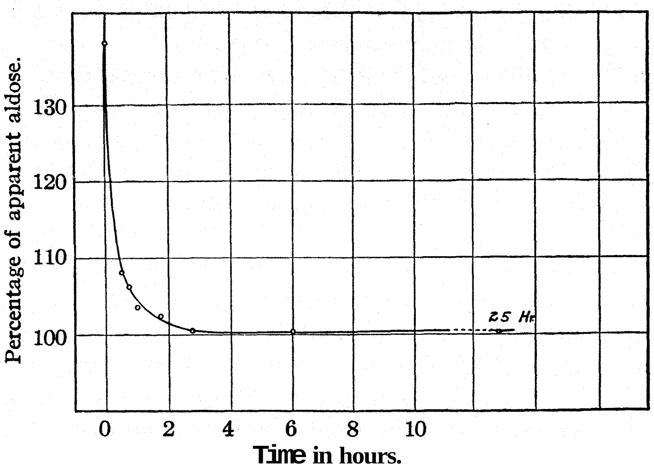

Fig. 3.—De-enolization of equilibrated mixture from tetramethyl glucose.

The rate of de-enolization of a more concentrated sugar solution was determined as follows and is plotted in Fig. 3. The conditions employed were one-fourth molar sugar solution in 3 N hydrochloric acid at 35°.

TABLE VIII

RATE OF "DE-ENOLIZATION" OF EQUILIBRATED MIXTURE FROM TETRAMETHYL GLUCOSE

Time, hours	Tetramethyl aldohexose, apparent %	Time, hours	Tetramethyl aldohexose, apparent %
0	138	1.75	102.7
.5	108.1	2.75	100.3
.75	106.3	6.0	100.5
1.0	103.3	25.0	100.4

From the preceding data it is seen that the constant value of 100% tetramethyl aldohexose is obtained on treatment of the equilibrated solution with acid and that, therefore, no methylated ketoses are present.

Absence of Methyl Alcohol.—The equilibrated solution and the de-enolized solution were examined for methyl alcohol according to customary methods with negative results.

Absence of Acid Substances.—The absence of acid substances was demonstrated in three ways. The accuracy of methods (2) and (3) was sufficient to show that not more than 1% of the sugar could have been transformed into acid substances.

(1) The neutral, equilibrated molar sugar solution was initially 0.035 N alkaline and thus the maximum limit of 3.5% conversion of the sugar into acid is set. The calcium could, of course, disappear as alcoholate,

(2) By removal of the calcium from the equilibrated solution as oxalate and titration of resulting solution.

(3) By alkali titration (phenolphthalein indicator) of the de-enolized solution, the original acidity of which was known.

Composition of Resultant Tetramethyl Aldohexose Solution, Optical Data.—By iodimetric data we have shown that the solution from tetramethyl glucose, equilibrated with alkali and de-enolized with acid, contains 100% aldohexose sugar. The optical data in the two following tables constitute evidence that tetramethyl glucose, $[\alpha]_D = +82°$, and tetramethyl mannose, $[\alpha]_D = +2.4°$, are present in equal amounts. No appreciable difference in specific rotation was found before and after de-enolization. Solutions of tetramethyl glucose on treatment with different concentrations of dilute alkali show widely differing initial polarimetric readings, but all reach the value for the equimolecular mixture, +42 ±1°. The same final specific rotation is reached on treating tetramethyl mannose under the same conditions and an equimolecular synthetic mixture of the two sugars maintains a stable specific rotation when treated with dilute alkali.

TABLE IX

POLARIMETRIC CHANGES OF METHYLATED GLUCOSE AND MANNOSE IN VARIOUS CONCENTRATIONS OF DILUTE ALKALI

Sugar	Normality of alkali	Time at 35°, hrs.	Observed reading	Time length	$[\alpha]^{20°}_D$
(a) Tetramethyl glucose	0 03 $Ca(OH)_2$	3	+37.39°	2 dcm.	+79.2°
		19	32.78	2 dcm.	69.4
		26	31.30	2 dcm.	66.3
		45	27.66	2 dcm.	58.6
		118	22.03	2 dcm.	46.6
		144	10.50	1 dcm.	44.5
		182	10.3	1 dcm.	43.6
(b) Tetramethyl glucose	0.04 $Ca(OH)_2$	7	35.65	2 dcm.	75.5
		29	29.25	2 dcm.	61.9
		50	26.00	2 dcm.	55.0
		70	24.05	2 dcm.	50.9
		96	22.75	2 dcm.	48.2
		121	21.85	2 dcm.	46.2
		169	20.87	2 dcm.	44.2
		192	20.8	2 dcm.	44.0
		250	20.5	2 dcm.	43.0
(c) Tetramethyl glucose	0.05 $Ba(OH)_2$	0.2	17.57	1 dcm.	74.4
		6	16.90	1 dcm.	71.6
		28	13.33	1 dcm.	56.4
		49	11.78	1 dcm.	49.9
		69	10.89	1 dcm.	46.1
		95	10.08	1 dcm.	42.7
		120	9.92	1 dcm.	42.0
		169	9.50	1 dcm.	40.2
		191	9.6	1 dcm.	40.6

TABLE IX (*Concluded*)

Sugar	Normality of alkali	Time at 35°, hrs.	Observed reading	Tube length	$[\alpha]^{20°}_D$
(*d*) Tetramethyl glucose	0.06 $Ba(OH)_2$	1.5	1834	1 dcm.	77.7
		6	16.76	1 dcm.	71.0
		265	12.50	1 dcm.	52.9
		59	10.71	1 dcm.	45.3
		76	10.32	1 dcm.	43.7
		102	999	1 dcm.	42.3
		127	9.80	1 dcm.	41.5
		176	9.65	1 dcm.	40.9
		193	9.6	1 dcm.	41.
(*e*) Tetramethyl mannose	0.06 $Ba(OH)_2$	7	2.31	1 dcm.	9.8
		17 5	452	1 dcm.	19.1
		24	5.70	1 dcm.	24.1
		31	657	1 dcm.	27.8
		43	7.76	1 dcm.	32 9
		55	8.45	1 dcm.	36.8
		75	9.43	1 dcm.	39 9
		92	9.72	1 dcm	41 2
		101	980	1 dcm.	41.5
		113	9.90	1 dcm.	41.9
		148	9.92	1 dcm.	42.0
(*f*) Equimolecular mixture of tetramethyl glucose and tetramethyl mannose	0.03 $Ba(OH)_2$	0.5	9.90	1 dcm.	41.9
		6	9.90	1 dcm.	41.9
		17.5	9 92	1 dcm.	42.0
		52.5	10.07	1 dcm.	42.6
		90	10.15	1 dcm.	43.0
		149	10.0	1 dcm.	42.3
		193	10.10	1 dcm.	42.8

From the data given in parts (d) and (*e*) of Table IX the rate of formation of tetramethyl mannose from tetramethyl glucose and of the reverse

TABLE X

RATE OF FORMATION OF TETRAMETHYL MANNOSE FROM TETRAMETHYL GLUCOSE AND THE REVERSE

(d)			(e)		
Interval, hours	Tetramethyl glucose, %	Tetramethyl mannose, %	Interval, hours	Tetramethyl glucose, %	Tetramethyl mannose, %
0	100.0	0	0	0	100.0
1.5	94.6	5.4	7	9 3	90.7
6	86.2	13.8	17.5	21.0	79.0
26.5	63.4	36.6	24	27.3	72.7
59	53.9	46.1	31	31.9	68.1
76	51.9	48.1	43	38.3	61.7
102	50.1	49.9	55	42.0	58.0,
127	49.1	50.9	75	47.1	52.9
176	48.4	51.6	92	48.7	51.3
193	49.0	51 0	101	49.1	50.9
			113	49.6	50.4
			148	49.7	50.3

under comparable conditions may be calculated. The data are given in Table X and are plotted in Fig. 4.

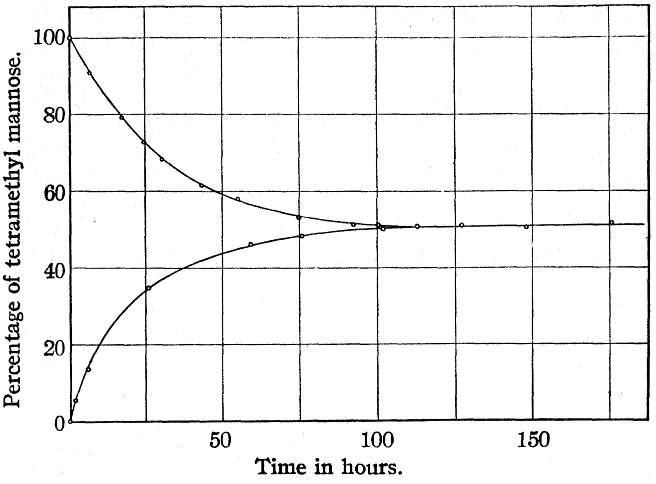

Fig. 4.—Interconversion of tetramethyl mannose and tetramethyl glucose.

Separation and Identification of the Anilides of Tetramethyl Glucose and Tetramethyl Mannose.—A weight of 35.43 g. of tetramethyl glucose was made up to 150 cc. molar solution with 0.0408 N barium hydroxide. This alkali was chosen in order that the metallic ion could be removed as barium sulfate. The resulting alkaline sugar solution was 0.0325 N alkaline. The determined density was 1.040. This solution was kept at 35° for 150 hours. The specific rotation at the end of this period was +43.4° (α = $20.51°, 2 dcm., c = molar) and the final iodine value, expressed as "apparent" aldohexose, was 138%.

The solution was then nearly "de-enolized." As some coloration occurs during this process it was deemed advisable not to carry this to completion. The molar sugar solution was diluted with sulfuric acid of such a concentration as to make the resulting solution fifth-molar sugar in 0.020 *N* sulfuric acid, allowance being made for the barium equivalent of the original solution. This diluted solution was heated rapidly in a 90° water-bath to 50° and then placed in a 50" oven for twelve hours. At the end of this period the iodine value was found to be 103% "apparent" aldohexose. The acid solution was neutralized at 40° by dropwise addition of *N*/10 barium hydroxide solution to slightly short of the neutral point and brought to neutrality by adding 0.5 g. of finely powdered barium carbonate and shaking vigorously. After standing for some time the solution was filtered and the residue washed with hot water. The filtrate was evaporated to constant weight at 25 mm. and 35°. A weight of 30.0 g. of sirup was obtained. Allowing for 2.8 g. of sugar withdrawn for samples and analysis, this represents a yield of 92%. An iodine titration of the distillate accounted for 1.5% additional if this iodine-consuming material be considered as aldohexose. Its presence in the distillate was probably due to a slight mechanical spray loss. The sirup was transferred to a 300cc. flask with absolute alcohol, removing by decantation 0.3 g. or 1% (not included in the 92% sirup figure) of brown, amorphous solid, insoluble in alcohol and ether, soluble in water and giving a test for the barium ion. A total of 95% of the original material was thus recovered.

The isolated sirup gave a specific rotation of + **42.4°** ($\alpha = +2.35°$, **0.943** dcm., c = **5.873)** and an iodine value of 112% "apparent" aldohexose. After subtracting **2.7** g. samples and analysis, the remaining **27.3** g. of sirup was dissolved in **81** cc. of absolute alcohol, making a **30%** solution, and an equal volume (8 moles) of purified, colorless aniline added. The solution was boiled gently under an air condenser for three hours. The color of the solution turned quite dark and appreciable aniline tar formation occurred which later interfered greatly with the crystallization of the anilides. On cooling of the reaction mixture and allowing this to stand, considerable crystallization occurred. The crystals were filtered and washed with aniline, 9.5 g. of crude material being obtained. On removal of the alcohol *in vacuo* a second crop of *5* g. of crystals was obtained. From the filtrate the aniline was removed *in vacuo,* a solid residue being obtained which was only slightly gummy. This residue and the two crops of crystals were recrystallized from absolute alcohol. All crops obtained in this work were dried *in vacuo* or over calcium chloride to constant weight. The mother liquors were thoroughly worked over. In this manner **27.4** g. of crystalline material was obtained in **13** crops.

The residual material, containing aniline tars, was dissolved in a small amount of alcohol and a considerable amount of **tar** removed by precipitation with ethyl ether and petroleum ether. After decantation from the tar, the solution was evaporated *in vacuo,* the residue dissolved in ethyl ether and a further quantity of tar removed by precipitation with petroleum ether. After removal of solvents, treatment with alcohol and refrigeration, **1.6** g. more of crystalline material was obtained in two crops. Working over the precipitated aniline tars yielded **0.1** g. of crystals.

The residual material was re-heated with aniline and alcohol and 0.6 g. more crystals obtained in two crops on working up the product with alcohol after removal of the aniline. The black, gummy material from the mother liquors of these two crops was dissolved in acetone, a relatively large volume of hot water added and steam passed through the solution. Some sepaiation of tarry matter was thus effected. After removal of the water in *vacuo,* the residue was re-heated with aniline and alcohol and **0.5** g. more crystals so obtained. The residue was then carried through another petroleum ether tar precipitation and **0.1** g. crystals obtained. Finally, a hot extraction with **9** parts of petroleum ether and **1** part of ethyl ether and evaporation of the extract gave **0.2** g. crystals. A final, black, gummy residue of **2.5** g. remained. A total of **30.4** g. of crystalline material was obtained. All of this had been crystallized from alcohol and dried to constant weight and represents an **85%** yield of anilide on the basis of the sirup used.

In order to separate and identify these anilides preliminary work was done with known pure material. It was found that the anilide of tetramethyl mannose was very appreciably more soluble in aniline than the anilide of tetramethyl glucose and a separation was effected on this basis. For identification of these compounds the following data are essential.

Tetramethyl mannose anilide has an equilibrated constant specific rotation in methyl alcohol of **8** degrees *laevo* ($c = 5$). This is obtained on standing for about forty hours or in a very short time on addition of **0.001%** of dry hydrogen chloride to the methyl alcoholic solution. On long standing in the acid methyl alcohol, the anilide shows a slow increase in the *dextro* direction, probably due to its known ease of hydrolysis. This is at the very slow rate of about one degree in twenty-four hours. Th[illegible]pound crystallizes from the solvents worked with in a mixture of what is probably [illegible] two alpha and beta forms, so that melting points and initial specific rotations are unreliable.

Tetramethyl glucose anilide mutarotates in methyl alcohol to the value of sty-nine degrees *dextro* ($c = 5$). Without a catalyst this value is obtained so slowly [illegible] to be unreliable. Addition of 0.001% of dry hydrogen chloride to the methyl alcohol equilibrated the solution in a short time, the final value remaining stable with the acid solution for at least twenty-two days. On one recrystallization from absolute ethyl alcohol, material that is evidently a pure form is obtained. This has a sharp melting point at 138° and shows in methyl alcohol the remarkably high specific rotation of +226° ($c = 2$). Without a catalyst this initial value changes downward so very slowly as to be a reliable constant.

The 30.4 g. of isolated crystals were laboriously separated by means of their varying solubilities in aniline and the crystals so separated were recrystallized from absolute ethyl alcohol. The tetramethyl glucose was removed largely first, as it was the less soluble in aniline and could readily be identified by its sharp melting point. The use of aniline and repeated evaporation *in vacuo* to dryness of aniline solutions introduced aniline tars again which occasioned the loss of some crystalline material.

A weight of 14.2 g. of pure tetramethyl glucose anilide was obtained in 12 crops. The melting point of each crop was determined and varied between 137 and 138.5". A mixed melting point of the material with a known sample of this anilide showed no depression. The initial specific rotation in methyl alcohol of the well mixed material was found to be +226° ($c = 1.998, a = +9.04°$, 2 dcm.) which lowered to the constant value of +58.3° ($c = 1.998, a = +2.33°$, 2 dcm.) on the addition of 0.001% of dry hydrogen chloride to the methyl alcohol.

A weight of 11.9 g. of pure tetramethyl mannose anilide was obtained in 6 crops. The well mixed material showed on equilibration a polarization value of −8° ($c = 5.000, \alpha = -0.38°$, 0.943 dcm.) in a methyl alcohol solution containing 0.001% of dry hydrogen chloride.

The unseparated material consisted of 0.5 g. of crystals which showed an equilibration polarization in methyl alcohol (3- 0.001% of HCI) of +38° ($c = 3.295, \alpha = +1.25°$, 1 dcm.). There remained 2.5 g. of gummy residual material, too dark to be polarized, and undoubtedly produced by repeated evaporation *in vacuo* of the aniline solutions. A loss in weight of 1.2 g. was suffered in separating the 30.4 g. of isolated crystals. The 26.1 g. of pure, separated crystals represents a separation yield of 86% on the basis of the isolated crystals.

Isolation and Identification of Tetramethyl Glucose and Tetramethyl Mannose.—Previous to the above separation, a rather qualitative run was made wherein the separated anilides were hydrolyzed to the sugars. These were isolated in crystalline condition and identified. The conditions used varied slightly from the previously described experiment.

Sixty cc. of molar tetramethyl glucose (14.2 g. of sugar) solution in 0.035 *N* (corrected for volume change) calcium hydroxide (PH 12.6) stood for ten days at 35°. These conditions were those used for d-glucose. The specific rotation (Table IX-b) dropped from +82 to +43° (constant) and the alkalinity was 0.008 N. The iodine value increased from 100 to 138% "apparent" aldohexose. The solution was diluted with hydrochloric acid to make a half molar solution in 3 N hydrochloric acid and stood for ten hours at 35°. The iodine value (Table VIII) rapidly decreased to 105 and then more slowly to the constant value of 100.4% of aldohexose.

The acid solution was neutralized with barium carbonate, the water removed *in vacuo*, the salt dried by distillation *in vacuo* with absolute ethyl alcohol and extracted with boiling ether. After removal of the ether, the resulting sirup, 10.9 g., gave an iodine value of 100.2% of aldohexose and a specific rotation of + 43.5' ($\alpha = +2.35$". I dcm., $c = 5.462$). As the specific rotation of the solution before acid treatment was +43°, it is seen that this constant is practically unchanged by the "de-enolization."

The sirup from the ether extract was dissolved in 32 cc. of absolute ethyl alcohol to make a 30% solution, an equal volume of purified aniline (8 moles) was added and the solution refluxed for three hours. On cooling this solution to room temperature and standing for some time, 3.6 g. of crystals was filtered off and washed with aniline. A second crop, 1.6 g., of crystals was obtained on removing the alcohol in *vacuo.* From the filtrate the aniline was removed in *vacuo* and the resulting solid, 10.3 g., was leached twice with 25 cc. of aniline. One and one-half g. of residual solid was obtained. The mixed anilides, 15.4 g. or 107% of crude yield, were thus roughly separated into two very nearly equal portions of aniline insoluble, 6.6 g., and the remainder aniline soluble material.

The bulk of the aniline from the two aniline extracts, kept separate, was removed in *vacuo.* The residue was dissolved in acetone and the solution poured into water to precipitate the anilide in finely divided condition. The resulting mixture was steam distilled for three hours, the anilide passing into solution quite rapidly. This solution was evaporated in *vacuo* and the cloudy sirup so obtained freed of the slight admixture of unhydrolyzed anilide by repeatedly taking up in absolute alcohol and filtering. Four and seven-tenths g. of the resulting sirup on nucleation with tetramethyl mannose yielded 1.7 g. of plated crystals, m. p. 42–49", $[\alpha]_D^{20} = +32°$ in methyl alcohol (*a* = + 1.11, 1 dcm. tube, $c = 3.490$). On recrystallization from low boiling petroleum ether the following constants were obtained and are compared with those obtained by R. D. Greene[9] of this Laboratory for highly purified tetramethyl mannose.

TABLE XI

IDENTIFICATION OF TETRAMETHYL MANNOSE

Constants of crystals from mixture	Known constants
M. p. 50–51°; $(\alpha)_D^{20} = +27.3°$ in methyl alcohol ($\alpha = +1.00°$, 1 dcm. tube, $c = 3.668$)	M. p. 50–51°; $(\alpha)_D^{20} = +27.5°$ ($c = 5.00$)

The aniline insoluble material, 6.6 g., was hydrolyzed in two portions. This hydrolysis was effected by adding to a 10% acetone solution of the anilide an equal volume of 10% hydrochloric acid. This solution was heated at 50° for one hour. It was then treated with an excess of barium carbonate and the aniline removed by two hours' steam distillation in presence of the excess barium carbonate. The aqueous solution was evaporated in *vacuo.* The salt residue was dried by distillation with absolute ethyl alcohol and extracted with boiling ether. The ethereal extract was evaporated in *vacuo.* On nucleation of the resulting sirup with tetramethyl glucose, 0.7 g. of plated crystals was obtained, m. p. 81–84', *(a),* = +85.2° in methyl alcohol (*or* = + 2.75°, 1 dcm. tube, $c = 3.226$). On recrystallization from petroleum ether containing a trace of ethyl ether the following constants were obtained and are compared with values obtained on pure tetramethyl glucose. The 89' melting point for tetramethyl glucose is that of the pure alpha form and is obtained only on repeated recrystallization.[23] The melting point of an ordinary preparation of this sugar runs somewhat lower.

TABLE XII

IDENTIFICATION OF TETRAMETHYL GLUCOSE

Constants of crystals from mixture	Known constants
M. p. 85–86°; $[\alpha]_D = +84.2°$ in methyl alcohol; ($\alpha = +2.67°$, I dcm. tube, $c = 3.172$)	M. p. 89' (highest recorded; determined in this Laboratory as +83° (c = 5)

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[23] Purdie and Irvine, *J. Chem. Soc.*, 85, 1054 (1904).

The authors wish to acknowledge their indebtedness to Professor F. C. Whitmore for his valuable advice and suggestions.

Summary

1. The predictions of the enediol theory of sugar interconversion as applied to the methylated sugars have been experimentally verified in a study of the action of dilute alkali on tetramethyl glucose. The facts determined are as follows.

a. No keto sugars are formed by the action of dilute alkali on tetramethyl glucose.

b. By the successive action of alkali and acid on tetramethyl glucose a mixture of tetramethyl mannose and tetramethyl glucose is obtained. Evidence was found that they are the only products of the reaction and are present in equimolecular amounts. Both of these closely related, epimeric sugars were isolated in pure crystalline condition and identified. The anilides of the sugars were formed in high yield, separated and identified.

c. Strong indication has been found for the presence of the monomethyl enediol common to tetramethyl glucose and tetramethyl mannose.

2. Experimental conditions have been found for the conversion of d-glucose by dilute alkali into a mixture of d-glucose, d-mannose and d-fructose with a negligible amount of saccharinic acid formation. The composition of the equilibrated solution has been determined.

3. The normal forms of tetramethyl glucose and tetramethyl mannose, prepared by methylation of the naturally occurring sugars, are mutually interconvertible and must, therefore, possess the same oxidic ring structure unless an improbable shifting of methyl groups occurs.

4. Evidence is cited that the mechanism of enol formation is not one of selective hydration and dehydration but rather simply that of tautomeric migration of a hydrogen atom.

EVANSTON, ILLINOIS

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

OPTICALLY ACTIVE HYPNOTICS

BY CHI-MIND HSUEH WITH C. S. MARVEL

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It is a well known fact that the physiological properties of many optical isomers are quite different even though their physical properties are the same in every respect except for their action on plane polarized light. The best known theory to explain the action of hypnotics is that of Overton and Meyer,[1] who have shown the close association of the physiological activity of hypnotics with their distribution coefficient for water and fat solutions. If optically active hypnotics were tested pharmacologically, some evidence in favor of or against this theory should result. If hypnotic action is largely due to the physical properties of the drug, then the dextro and laevo isomers of any hypnotic compound should have the same physiological action, which might or might not be different from that of the racemic substance. On the other hand, if the physiological properties are largely dependent on the molecular structure of the compound, the two active isomers would be expected to have different hypnotic actions and the racemic substance would fall between in its behavior.

The commonest hypnotics in practical use are the derivatives of barbituric acid. The simplest known derivative of this group with a fair degree of hypnotic action and an asymmetric alkyl group is ethyl-*sec.*-butylbarbituric acid. This substance was prepared by the method of Shonle and Moment.[2] The compound which was obtained melted at 197° instead of 155–157° as given by them. Its purity was demonstrated by analyses. No convenient method of resolution was found as the barbituric acid derivative did not seem to be a strong enough acid to form stable salts with the alkaloids or other optically active amines which were available.

Another possible method of obtaining an optically active barbituric acid is to prepare an active alcohol, convert it successively to the bromide, then to the alkylmalonic ester derivative and finally to the barbituric acid derivative. Since secondary octyl alcohol (octanol-2) is readily available and quite easily resolved by Kenyon's[3] procedure, it was decided to use it as a starting point. It was thought that ethyl-*sec.*-octylbarbituric acid should have a sufficiently strong physiological action for the purpose of determining the difference in the action of the optical iso-

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[1] Overton, "Studien über die Narkose, zugleich ein Betrag zur Allgemeinen Physiologie," Jena, G. Fischer, 1901, p. 70; Meyer, *Arch. exp. Path. Pharmakol.*, 42, 109, 119 (1901).

[2] Shonle and Moment, THIS JOURNAL, 45, 243 (1923).

[3] Kenyon, *J. Chem. Soc.*, 121, 2540 (1922); "Organic Syntheses," John Wiley and Sons, Inc., New York, 1926, Vol. VI, p. 68.

mers. Accordingly the three optical isomers of this substance were prepared.

The active *sec.*-octyl alcohols used for the syntheses had the rotations of ± 9.9°. The bromide of the inactive form was made first and it was found that slightly better yields could be obtained from the alcohol and phosphorus tribromide than from the alcohol and hydrobromic acid either with or without the addition of sulfuric acid. Accordingly the active bromides were made from the active alcohols by this same procedure. The bromides thus obtained had rotations of +34.05° and −34.25°, which are higher than reported for the same bromides made by the hydrobromic acid method. Levene and Mikeska[4] report a rotation of +14.56° for the dextro isomer and Pickard and Kenyon[5] report rotations of ±27.5 for the bromides.

The bromides were allowed to react with an excess of the sodium derivative of diethyl ethylmalonate in order to obtain the best possible yields of diethyl ethyl-*sec.*-octylmalonate. The rotations of the active esters were +8.22° and −8.07°. There was no change in the sign of rotation in going from the bromide to the malonic ester derivative.

The barbituric acid derivatives were prepared by the usual procedure of condensing the malonic ester derivative with urea in the presence of sodium ethylate. The inactive derivative melted at 126–127°, whereas the active isomers melted at 107°. The rotations of the active forms were +7° and −7.02°. It is not certain that some racemization did not occur in these different steps. However, the close agreement between the rotations of the dextro and the laevo forms showed that they were of the same degree of purity and that valid conclusions could be drawn from pharmacological tests made with these substances.

The pharmacological tests were carried out by Mr. H. C. Spruth at the Abbott Laboratories.[6] The minimum effective dose (M. E. D.) and the minimum fatal dose (M. F. D.) were determined on albino rats according to the method of Nielsen, Higgins and Spruth.[7] These data are recorded in Table I.

The errors in data of this kind are sometimes as much as 10%. However, since the determinations were made by one worker they may be safely used for comparison.

These results show that there is practically no difference in the physiological activity (either hypnotic action or toxicity) of the dextro and laevo isomers. This tends to confirm the view that physical properties are the most important factors in determining the activity of an hypnotic of this

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[4] Levene and Mikeska, *J. Biol. Chem.*, 59,478 (1924).

[5] Pickard and Kenyon, Ber., 45, 1593 (1912).

[6] The authors desire to express their thanks to Mr. Carl Nielsen and Mr. Henry C. Spruth of the Abbott Laboratories for their assistance in this investigation.

[7] Nielsen, Higgins and Spruth, *J. Pharmacol.*, 26, 371 (1928).

series. There seems to be no difference between the effect of the active form and of the racemic form.

TABLE 1

PHARMACOLOGICAL DATA ON THE *d*-, *l*- AND *dl*-5-ETHYL-5-*sec*.-OCTYLBARBITURIC ACIDS

	M. F. D. in mg. per g. of rat	Ratio of toxicity, barbital = 1	M. E. D. in mg. per g. of rat	Ratio of efficiency, barbital = 1	Safety margin, %
dl-isomer	1.90"	0.16	0.37	0.61	80.5[c]
d-isomer	1.85	.17	.38	.59	79
1-isomer	[b]	..	.36	.62	..

[a] The toxicity figures were determined with 10% solutions of the sodium salts.

[b] A definite M. F. D. could not be determined for this isomer because of the small supply of material available and certain inconsistencies in the results, but from the work done it may be said that the toxicity is approximately the same as that of the other two compounds.

[c] The safety margin is the difference between the M. F. D. and the M. E. D. expressed in percentage of the M. F. D.

Experimental Part

dl-2-Bromo-octane.—Three different procedures were employed in this preparation, one using the alcohol with sulfuric acid and hydrobromic acid, one using only hydrobromic acid and the alcohol, and the last using phosphorus tribromide with the alcohol.

Hydrobromic Acid–Sulfuric Acid Method.—One mole (130 g.) of crude capryl alcohol (b. p. 165–170°), 2 moles (340 g.) of 48% hydrobromic acid solution and 0.25 mole (25 g.) of concd. sulfuric acid were refluxed for about five hours and then steam distilled. The bromide layer was separated from the water, washed successively with ice-cold concd. sulfuric acid, water, sodium carbonate solution and finally with water, and dried over calcium chloride. A yield of 95 g. (49% of the theoretical amount), b. p. 71–73" at 14 mm., was obtained on distilling the product.

Hydrobromic Acid Method.—The same quantities of alcohol and hydrobromic acid without the sulfuric acid were used and the mixture was refluxed as before. The bromide-alcohol mixture was distilled, separated from the water layer and again treated with two moles of hydrobromic acid solution. The final yield of purified product was 10% lower than when a little sulfuric acid was used.

Phosphorus Tribromide Method.—In a 2-liter, three-necked flask, fitted with a mechanical stirrer, a thermometer reaching nearly to the bottom of the flask and a separatory funnel, was placed 130 g. of crude capryl alcohol (b. p. 165–170°). The stirrer was started and after cooling the alcohol to −5°, 298 g. of phosphorus tribromide was added drop by drop at such a rate that the temperature did not go above +5°. This required about two hours. The mixture was allowed to stand overnight and thus gradually come to room temperature. The thermometer was removed and a tube to carry off fumes of hydrogen bromide was put in its place. The mixture was heated on a steam-bath for one hour. Then to it was added first, slowly, about 300 cc. of cold water and then about 150 cc. of ether to aid in the separation of the bromide. The ether solution was separated, washed with sodium carbonate solution and water, dried over calcium chloride and distilled. The yield of bromide, b. p. 71–73' at 14 mm., was 98 g. (51% of the theoretical amount). The low yields by all of the methods can undoubtedly be traced in part to the fact that the capryl alcohol was prepared by the distillation of a mixture of castor oil and sodium hydroxide and was purified only by fractional distillation.

The bromide boils at 61° at 3 mm., 66° at 6 mm., 72° at 14 mm.; $d_4^{25} = 1.0878$; $n_D^{25} = 1.4442$, M_D, calcd., 46.92; obs. 47.00.

***l*-2-Bromo-octane.**—The procedure used in this preparation is the same as described for the inactive bromide by the phosphorus tribromide method. From 76 g. of d-octanol-2 ($[\alpha]^{25}_{D}$ = +9.9°) and 174 *g.* of phosphorus tribromide, there was obtained 91 g. (80% of the theoretical amount) of l-2-bromo-octane, b. p. 60° at 3 mm., 71° at 14 mm.; d^{25}_{4} = 1.0982; n^{25}_{D} = 1.4475; M_D, calcd., 46.92; obs., 46.87; $[\alpha]^{25}_{D}$ = —34.25'.

Anal. (Stepanoff). Subs. 0.1964 g.: 10.1 cc. of 0.1000 *N* $AgNO_3$. Calcd. for $C_8H_{17}Br$: Br, 41.17. Found: 41.18.

d-2-Bromo-octane.—From 55 g. of 1-octanol-2 ($[\alpha]^{25}_{D}$ = —9.9") and 126 *g.* of phosphorus tribromide, there was obtained 66 g. (80% of the theoretical amount) of *d*-2-bromo-octane. The physical constants were identical with those of the laevo isomer except for the rotation, $[\alpha]^{25}_{D}$ = +34.2°.

***dl*-Diethyl Ethyl-*sec.*-octylmalonate.**—The common procedure for the preparation of a substituted malonic ester was followed[8] It was found by experiment that the best yields were obtained when a rather large excess of the sodium derivative of diethyl ethylmalonate was used. The amounts of reagents used were as follows: 150 cc. of absolute alcohol, 8.65 g. of sodium, 94 g. of diethyl ethylmalonate and 48 g. of *dl*-2-bromo-octane. The yield of ester was 32.5 g. (43% of the theoretical amount), b. p. 135–140° at 3 mm., 137–142° at 6 mm., 158–165° at 17 mm., 170–175° at 27 mm.; d^{25}_{4} = 0.9434; n^{25}_{D} = 1.4365; M_D, calcd., 84.04; obs., 83.75.

Anal. Subs., 0.1904: CO_2, 0.4740; H_2O, 0.1825. Calcd. for $C_{17}H_{32}O_4$; C, 68.00; H, 10.67. Found: C, 67.80; H, 10.64.

***d*-Diethyl Ethyl-*sec.*-octylmalonate.**—By the same procedure, from 230 cc. of absolute alcohol, 11.8 g. of sodium, 129 g. of diethyl ethylmalonate and 66 g. of *d*-2-bromo-octane, there was obtained 42 g. (41% of the theoretical amount) of d-ester, b. p. 137–138° at 3 mm.; d^{25}_{4} = 0.9323; n^{25}_{D} = 1.4370; M_D, calcd., 84.04; obs., 83.95; $[\alpha]^{25}_{D}$ = +8.22°.

Anal. Subs., 0.2000: CO_2, 0.4971; H_2O, 0.1925. Calcd. for $C_{17}H_{32}O_4$; C, 68.00; H, 10.67. Found: C, 67.91; H, 10.69.

***l*-Diethyl Ethyl-*sec.*-octylmalonate.**—From 300 cc. of absolute alcohol, 16.3 g. of sodium, 177 g. of diethyl ethylmalonate and 91 g. of *l*-2-bromo-octane, there was obtained 59 g. (41% of the theoretical amount) of the l-ester; $[\alpha]^{25}_{D}$ = —8.07'. The other physical constants were identical with those of the dextro isomer.

dl-5-Ethyl-5-sec.-octylbarbituric Acid.—A solution of 23.25 g. of diethyl ethyl-*sec.*-octylmalonate, 5.37 g. of sodium and 6.7 g. of dry urea in 150 cc. of absolute alcohol (dried with magnesium methylate) was refluxed in an oil-bath held at 105–110° for one hour. The condenser was then set for distillation and the alcohol was removed by distillation. This required about three hours. The reaction mixture was held at the temperature of 105–110° for about an hour after the alcohol was removed. The contents of the flask were then dissolved in about 200 cc. of water and the solution was acidified with concd. hydrochloric acid. The barbituric acid derivative separated as an oil which solidified when the mixture was allowed to stand overnight or when it was cooled in an ice-bath. This crude product was filtered, crushed in a mortar and washed thoroughly with water. It was then recrystallized from about 300 cc. of 60% acetic acid from which it separated in long needles. The yield was 10 g. (48% of the theoretical amount) of a product, m. p. 126–127°.

AM. (Kjeldahl). Subs. 0.2000: 14.6 cc. of 0.1000 *N* HCl. Calcd. for $C_{14}H_{24}O_3N_2$: N, 10.47. Found: 10.22.

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[8] Adams and Kamm, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 11.

d-5-Ethyl-5-*sec*.-octylbarbituric Acid.—The procedure was identical with that described above. However, the yield was only 26.5% of the theoretical amount. The product melted at 107°; $[\alpha]^{25}_{D} = +7°$ (2 g. in 15 cc of alcohol).

And. Subs. 0.2000: 14.8 cc. of 0.1000 N HCl. Calcd. for $C_{14}H_{24}O_3N_2$: N, 10 47. Found: 10.36.

l-5-Ethyl-5-*sec*.-octylbarbituric Acid.—This was prepared in exactly the same manner and the yield was identical with that of the dextro compound, $[\alpha]^{25}_{D} = -7\ 02°$ (2 g. in 15 cc. of alcohol). In other respects it was identical with the dextro isomer.

Summary

1. The d-, l- and dl-isomers of 5-ethyl-5-*sec*.-octylbarbituric acid have been prepared.

2. Pharmacological tests show that there is almost no difference in physiological action between the d- and l-isomers.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

CATALYSIS WITH COPPER IN THE ULLMANN REACTION

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Professor Fritz Ullmann[1] discovered that the addition of copper catalyzed the reaction of aryl halides with aryl amines or N-acyl aryl amines to form N-aryl aryl amines and of salts of phenols with aryl halides to form di-aryl ethers. A high boiling solvent (nitrobenzene or phenol) was used and potassium carbonate added to neutralize the halogen acid formed.

In most of the later work a special copper was used as a catalyst. This "Naturkupfer C," is a finely divided product obtained by grinding metallic copper under oil between mill stones. However, in some cases other forms of copper and even copper compounds gave equally good results. There has been little information available to indicate whether the reaction involved a case of heterogeneous or homogeneous catalysis, as to what was the real catalyst and why there was such a variation in the results obtained in using different reactants and different samples of copper or copper compounds.

A rather intensive study has been made of the reaction of phenyl bromide

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[1] (a) Ullmann, Ber., 36, 2382 (1903); (b) Ullmann and Sponagel, Ber., 38, 2211 (1905); (c) Irma Goldberg, *Ber.*, 39, 1691 (1906); (d) Ber., 40, 4541 (1907); (e) Ullmann, *Ann.*, 355, 312 (1907); (f) British patents: 2949 (1912), C. *A.*, 7, 2477 (1913); 16,272 (1910), *C. A.*, 5,3121 (1911); 16,440 (1910), *C.* A., 5,3165 (1911); (g) French patent: 418,210 (1910), *C.* A., 6, (1912); (h) German patents: 173,523 (1905), C. A., 1, 513 (1907); 185,663 (1906), C. *A.*, 2,351 (1908); 187,870 (1906), C. A., 2, 602 (1908); 224,982 (1909). C. *A.*, 5, 213 (1911); 238,106 (1910), C. *A.*, 6, 1680 (1912); 248,999 (1910), *C. A.*, 6,2851 (1912).

with N-acetyl-p-toluidine in order to obtain more precise information with regard to the course and mechanism of the reaction which bears Ullmann's name. The yield of N-phenyl-p-toluidine resulting from the reaction of phenyl bromide and N-acetyl-p-toluidine in nitrobenzene varied from 8 to 43% depending upon whether various forms of metallic copper or copper salts were used. The experimental procedure is given below and a summary of the results under numbers 1–14 inclusive of the table.

TABLE I

THE PREPARATION OF *N*-PHENYL-*p*-TOLUIDINE

Expt.	Catalyst[a]	Solvent	Time, hours	Temp., °C.	Yield, %	Checks	Procedure
1	A	$C_6H_5NO_2$	4	200	38 ± 5	3	1
2	B	$C_6H_5NO_2$	4	200	23 ± 1	2	1
3	C	$C_6H_5NO_2$	4	200	36 ± 2	3	1
4	D	$C_6H_5NO_2$	4	200	25 ± 2	3	1
5	F	$C_6H_5NO_2$	4	200	9 ± 1	3	1
6	H	$C_6H_5NO_2$	4	200	25 ± 5	3	1
7	I	$C_6H_5NO_2$	4	200	23 ± 2	3	1
8	J	$C_6H_5NO_2$	4	200	30 ± 1	3	1
9	K	$C_6H_5NO_2$	4	200	34 ± 3	3	1
10	L	$C_6H_5NO_2$	4	200	22 ± 1	2	1
11	M	$C_6H_5NO_2$	4	200	15 ± 2	3	1
12	N	$C_6H_5NO_2$	4	200	15	1	1
13	O	$C_6H_5NO_2$	4	200	11	1	1
14	P	$C_6H_5NO_2$	4	200	30	1	1
15	A	$C_{10}H_{12}$	4	200	21	1	1
16	A	$C_{10}H_{12}$	8	200	30	1	1
17	A	$C_{10}H_{12}$	24	200	42	1	1
18	A	$C_{10}H_{12}$	48	200	50	1	1
19	A	$C_{10}H_{12}$	148	200	Tat	1	1
20	A	$C_6H_5NO_2$	4	190	21	1	1
21	A	$(C_6H_5)_2O$	4	190	11	1	1
22	A	$(C_6H_5)_2O$	4	200	24	1	1
23	A	$C_{10}H_{12}$	4	190	9	1	1
24	A	$(C_6H_5)_2O$	4	210	39	1	1
25	A	$C_{10}H_{12}$	4	200	5	1	2
26	A	None	15	B. p.	84	1	3
27	A	None	25	B. p.	90	1	3
28	J	None	16	B. p.	87	1	3
29	E	None	15	B. p.	90	1	3
30	A	$C_{10}H_{12}$	4	200	0	2	4
31	A	$C_{10}H_{12}$	4	200	0	2	5
32	A	$C_6H_5NO_2$	4	200	0	2	4
33	A	$C_6H_5NO_2$	4	200	0	2	5
34	A	None	4	B. p.	0	2	6
36	A	None	4	B. p.	0	2	7
36	A	None	4	B. p.	35 ± 10	4	8
37	A	None	4	B. p.	35 ± 10	4	9 (air)
38	A	None	4	B. p.	13 ± 3	3	9 (CO_2)

TABLE I (*Concluded*)

Expt.	Catalyst[a]	Solvent	Time, hours	Temp., °C.	Yield, %	Checks	Procedure
39	E	None	4	B. p.	0	4	9 (CO_2)
40	A'	None	4	B. p.	0	2	9 (CO_2)
41	E	None	4	B. p.	20 ± 3	4	9 (air)
42	A'	None	4	B. p.	20 ± 3	4	9 (air)

[a] CATALYSTS.—(A) "Naturkupfer C." (A') The "Naturkupfer C" was washed with ether to remove grease, reduced at a dull red heat in a stream of hydrogen and sealed off in the tube in which it was reduced. (B) Metallic copper from the reduction of cupric oxide. (C) Metallic copper from the reduction of cuprous oxide. (D) Metallic copper produced by the action of zinc dust on a concentrated solution of copper sulfate. The copper was washed with dilute hydrochloric acid to remove the zinc and with water until free of acid. It was preserved under water and before use was dried with alcohol and ether. (E) A piece of sheet copper 5 X 5 cm. was washed with ether to remove grease, then with hydrochloric acid to remove the oxide. The acid was washed out with water and the copper dried with alcohol and ether. (F) Commercial cupric chloride crystals were heated to 120° to drive out the water. (G) Commercial cuprous chloride. (H) Commercial cupric bromide. (I) Cuprous bromide, prepared from copper sulfate, potassium bromide and copper wire. (J) Commercial cuprous iodide. (K) Cuprous iodide plus iodine crystals. (L) Cupric oxide was prepared by heating crystalline copper nitrate in a large test-tube until no more brown fumes were evolved. (M) Cuprous oxide was prepared by the reduction of Fehling's solution with dextrose. (N) Commercial cupric acetate. (O) Commercial copper tartrate. (P) Anhydrous copper sulfate.

Procedure 1.—Eight g. (0.05 mole) of acetyl-p-toluidine, 8 g. (0.05 mole) of bromobenzene, 5 g. of potassium carbonate, 40 cc. of solvent and the catalytic agent were placed in a 125cc. flask (with a long neck to act as a reflux condenser) and stirred while being heated in the thermostat. After the reaction time had elapsed, the flask was removed from the bath and allowed to cool to room temperature. Almost all of the unreacted acetyl-p-toluidine crystallized out. (In order to determine the amount of unreacted material, this was recrystallized from hot water, dried and weighed.) After filtration the solvent was removed by steam distillation. The residue in the flask was shaken with 50 cc. of ether to dissolve the acetylphenyl-p-toluidine, the ether layer filtered and the ether removed by distillation. The free amine was obtained by refluxing with 40 cc. of 95% ethyl alcohol and 5 g. of potassium hydroxide for one hour. The hot alcoholic solution was poured into 300 cc. of water and allowed to coagulate sufficiently to make filtration easy. It was dried and weighed.

The reaction is very sensitive to the presence of traces of water and all reagents must be quite dry if a good yield is to be obtained. The yield also depends upon whether nitrobenzene, tetrahydronaphthalene or diphenyl ether is used as a reaction medium (Expts. 1, 15, 22); upon the duration of the heating (Expts. 15, 16, 17, 18, 19); upon the reaction temperature (Expts. 1 and 20, 15 and 23, 21, 22 and 24); and upon the amount of solvent (Expts. 15 and 25). Procedure 2 was the same as 1 except that 80 cc. instead of 40 cc. of solvent was used.

The failure to obtain higher yields was not due to side reactions which consumed one or the other of the reactants because quantities of both phenyl bromide and acetyl-*p*-toluidine were present in the reaction mixture after the synthetic reaction stopped. The low yields could not be explained on the basis of a reversible reaction because the N-acetylphenyl-p-toluidine could not be converted into phenyl bromide and acetyl-*p*-toluidine under the experimental conditions during the synthesis. The use of more copper at the beginning of the synthesis or the addition of a second portion of copper after the first portion ceased to function did not result in increased yields of product. The only conclusion that can be reached from these facts is that the synthetic reaction ceased because the conditions in the reaction mixture became such that a dispersion of catalyst could no longer be maintained. That is to say, the formation of by-products resulted in such a solution that the catalyst was precipitated and further dispersion of copper prevented. The variation of the yields of secondary amine with variations in kind and amount of solvent, source of catalyst and concentration of water are in agreement with this conclusion, for the time required for the solution to become "poisoned" would depend upon the solvent and its impurities, such as water, and upon the impurities and catalysts for side reactions introduced along with the copper from various sources.

The picture of the reaction would then include the fact that almost any copper or copper compound may be used as a source of catalyst but that the true catalyst becomes dissolved or dispersed in the reaction mixture and catalyzes the reaction until it is thrown out of solution due to the development of a sufficient concentration of impurities.

To test out these ideas the reaction was then run without a solvent even though all previous workers had recommended the use of one. The yields so obtained were more than double the best yields obtained with the best solvent (Runs 26–29 inclusive).

Procedure 3.—Four g. of acetyl-p-toluidine, 4 g. of bromobenzene, 2.5 g. of potassium carbonate and the catalyst were placed in a 50cc. Erlenmeyer flask fitted with a 30cm. reflux air condenser, and boiled vigorously on an electric hot-plate. After the reaction time had elapsed, 5 cc. of water was added and steam bubbled through to remove the excess bromobenzene. After cooling, the product was extracted with 30 cc. of ether, filtered, the ether evaporated off and the *N*-acetylphenyl-*p*-toluidine hydrolyzed as in Procedure 1.

The question then arises as to whether the catalyst is a dispersed solid or is in true solution and, if the latter, which one or combination of reactants is responsible for carrying the copper or copper compound into a soluble form. The following experiments were carried out.

Procedure 4.—Eight g. of acetyl-p-toluidine, 5 g. of potassium carbonate, 40 cc. of solvent and the catalyst were stirred while being heated for two hours in the thermo-

stat. The hot mixture was filtered to remove the copper, and to the liquid were added 8 g. of bromobenzene and 5 g. of potassium carbonate (thereafter Procedure 1).

Procedure 5.—The catalyst, 40 cc. of solvent, 8 g. of bromobenzene and 5 g. of potassium carbonate were stirred while being heated in the thermostat for two hours. The hot solution was filtered to remove the copper and to it were added 8 g. of acetyl-*p*-toluidine and 5 g. of potassium carbonate (Procedure 1 thereafter).

Procedure 6.—The catalyst, 8 g. of acetyl-p-toluidine and 5 g. of potassium carbonate were heated together at about 200° for two hours in a 50cc. Erlenmeyer flask. The product was dissolved in dry benzene, the copper filtered off and the benzene evaporated. Five g. of potassium carbonate and 8 g. of bromobenzene were added (thereafter Procedure 3).

Procedure 7.—The catalyst was refluxed with 8 g. of bromobenzene and 5 g. of potassium carbonate for two hours. The mass was dissolved in a little benzene and filtered to remove the copper. After distilling off the benzene, 8 g. of acetyl-p-toluidine and 5 g. of potassium carbonate were added (thereafter Procedure 3).

Procedure 8 was the same as 6 except that the material after heating was dissolved in boiling absolute alcohol instead of benzene. The extract was red in color. When 95% alcohol was used for the extraction, the dried, extracted material gave lower yields of *N*-phenyl-*p*-toluidine than that extracted with absolute alcohol. This indicates that the deleterious effect of water upon the Ullmann reaction is due to its partially destroying the intermediate copper compound.

The results of these experiments (see Table I) showed very conclusively that none of the reactants had any effect upon copper in converting it into a catalyst except the acetylated amine. This reacted with either Naturkupfer C or sheet copper to form an alcohol soluble compound.

This alcohol soluble compound was active in promoting the reaction of bromobenzene and N-acetyl-p-toluidine. If air was excluded during the fusion of the acetylated amine over sheet copper the alcoholic extract contained no catalyst. However, the exclusion of air from the fusion of N-acetyl-p-toluidine with Naturkupfer C (Run 38) did not entirely prevent the formation of an alcohol soluble catalyst. However, Naturkupfer C failed to yield a catalyst if before fusion with the acetylated amine it was washed with ether to remove grease and heated in a stream of hydrogen to remove adsorbed oxygen (Expt. 40). Both sheet copper and the washed and deoxygenated Naturkupfer C yielded a catalyst if air was used as in Procedure 9 (Expts. 41, 42).

Procedure 9.—The catalyst was fused with 8 g. of acetyl-p-toluidine in a 50cc. Erlenmeyer flask at about 200° for two hours. It was dissolved in boiling absolute alcohol and filtered. The alcohol was boiled away and 8 g. of bromobenzene and 5 g. of potassium carbonate were added (thereafter Procedure 3). In order to carry out this reaction in an atmosphere of carbon dioxide, the gas was passed through the flask containing the catalyst and acetyl-p-toluidine in order to drive out the air. The pressure was lowered to 30 mm. and the flask was heated at 200° for two hours. Air was allowed to enter, alcohol added, and the process carried out as above. If the mixture was heated so high that the acetyl-toluidine began to distil, only tarry matter was formed. If the temperature was much below 200°, a long time was required for the reaction.

It is clear, then, that the catalyst for the Ullmann reaction is formed by the reaction of copper with the acetylated amine in the presence of air, and that it is, in the case investigated, an alcohol soluble compound which is either red in color or associated with such a compound. The fact that copper reacts with oxygen and ammonia to form $Cu(NH_3)_4(OH)_2$[2] perhaps gives a hint as to the constitution of the catalytically active copper derivatives of the acetylated amine.

In order to obtain the maximum yield of N-phenyl-p-toluidine, at least 0.1 g. of copper must be used for 0.05 mole of reactants. In order to be sure of having enough, 0.3 g. was used in most of the preparations. The alcohol extract containing the true catalyst used in Expts. 36 and 37 contained the equivalent of approximately 2 milligrams of copper. It may be noted that the yields were considerably lower in these cases than in those where metallic copper was present during the reaction of the N-acetyl amine and the phenyl bromide. This is probably due to the fact that the true catalyst is gradually destroyed during the course of the reaction and if no metallic copper is present there is no replenishment of the supply of true catalyst by solution of metallic copper. The use of only a portion of the alcoholic extract of Procedure 8 resulted in lower yields than were obtained by the use of the whole extract.

Magnesium oxide, calcium carbonate, *p*-toluidine and quinoline were substituted for the potassium carbonate in the procedure for the preparation of N-phenyl-N-acetyl-p-toluidine but no reaction ensued. All attempts to use powdered metallic silver, silver iodide or silver oxide in place of copper gave negative results as reported by Ullmann. Naturkupfer C apparently does not promote the reaction of butyl or phenyl bromide with phthalimide. However, a small amount of diphenylamine was formed by the reaction of acetamide with phenyl bromide. N-phenyl-o-toluidine (b. p., 304–305°, corr.) was prepared in 70% yield by the reaction of 0.2 mole of N-acetyl-o-toluidine with 0.2 mole of phenyl bromide *without* a solvent in the presence of Naturkupfer C. The N-acetyl-N-phenyl-o-toluidine obtained as an intermediate apparently had not previously been prepared. It has a melting point of 77.5°, the crystals

TABLE II

THE PREPARATION OF DIPHENYL ETHER

Expt. no.	Catalyst	Solvent	Time, hours	Temp., °C.	Yield, %	Checks	Procedure
43	A	C_6H_5OH	2	210	70	2	10
44	A	C_6H_5OH	3	210	60	2	11
45	None	C_6H_5OH	3	210	0	1	11
46	A	None	3	210	0	2	11
47	E	C_6H_5OH	4	210	50	1	11
48	E	C_6H_5OH	5	210	30	2	12 (air)
49	E	C_6H_5OH	5	210	0	2	12 (CO_2)

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[2] Yamasaki, *Science Repts.* Tokoku Univ., 9,169 (1920); Dawson, *Z. physik. Chem.*, 69, 110 (1909).

being triclinic. Templeton[3] was unable to prepare N-phenyl-*o*-toluidine using nitrobenzene as a solvent. His negative results have been checked.

A summary of the results obtained in using copper as a catalyst for the reaction of potassium phenoxide and phenyl bromide is shown in Table II, the experimental procedures being given below.

Procedure 10.—Four g. of metallic potassium was dissolved in 17 g. of melted phenol, keeping the mass hot enough so that it remained liquid. Some charring took place. To this were added 15.8 g. of bromobenzene and the catalyst and the mixture was heated under a reflux condenser in an oil-bath. After cooling, 120 cc. of water and some potassium hydroxide were added to dissolve the phenol and phenoxide. The diphenyl ether was separated, dried with anhydrous sodium sulfate and distilled. Depending on the yield of diphenyl ether obtained, the layer containing it might be on top or below.'

Procedure 11.—Thirteen g. of potassium phenoxide, 15.8 g. of bromobenzene, 10 g. of phenol and the catalyst were heated together under a reflux air condenser in an oil-bath. The products were separated according to Procedure 10.

Procedure 12.—The catalyst and 10 g. of phenol were heated together at 150–160° for two hours while air was slowly passed through the mixture. The phenol was poured away from the catalyst, and to it were added 15.8 g. of bromobenzene and 13 g. of potassium phenoxide. Thereafter the procedure was the same as in number 10, carbon dioxide being used as in Procedure 9.

These experiments show that air is necessary for the formation of an active catalyst from copper and phenol as it is in the case of N-acetyl-*p*-toluidine. Contrary to the experience of Ullmann, there was found to be no great difference in the yield of diphenyl ether irrespective of whether the phenoxide was made by the reaction of potassium hydroxide *or* phenol or by the reaction of potassium and phenol as recommended by Ullmann. It is, however, necessary that excess phenol be used as a solvent for the reaction and that water be excluded from the reaction mixture. The true catalyst appears to be a combination of phenol and copper which is sensitive to the presence of water.

Preparation and Purity of Reagents

Acetyl-p-toluidine and Acetyl-o-toluidine were prepared by the action of acetic anhydride on the corresponding toluidines. The products after recrystallization had melting points of 150.5" (corr.) and 110° (corr.), respectively.

The bromobenzene was dried over calcium chloride; b. p., 154–155.5° (corr.).

The potassium carbonate was dried at 200° for ten hours.

The solvents were dried with calcium chloride and distilled: nitrobenzene, b. p., 209.5–211° (corr.); diphenyl ether, b. p., 258–261° (corr.); tetrahydronaphthalene, b. p., 205–208° (corr.).

The potassium phenoxide was prepared by dissolving potassium hydroxide in fused phenol. The water and excess phenol were removed by distillation under a pressure of 30 mm. at 210° for three hours.

The other reagents used were the usual commercial products.

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[3] Templeton, Ph. D. *Dissertation*, Wisconsin, 1924,

[4] Ullmann and Sponagel, Ann., 350, 83 (1906).

Summary

It has been found that the addition of almost any sample of metallic copper or copper compound will catalyze the reaction of phenyl bromide and N-acetyl-*p*-toluidine. The yield of product varies and is a function of the particular sample of copper or copper compound used. It also varies with the kind and amount of solvent as well as with the dryness of the reagents.

The use of a solvent as by former workers is quite disadvantageous, the yields without a solvent being more than twice as great as under the optimum conditions with a solvent. N-phenyl-o-toluidine could not be obtained using nitrobenzene as a solvent but was easily obtained in 70% yield without a solvent.

The low yields in a solvent are not due to a reversal of the reaction or to side reactions but are apparently due to the fact that conditions in the reaction mixture become such that it is no longer possible for a concentration of the true catalyst to be maintained. Direct evidence on this point has been obtained with respect to the injurious action of water.

It has been shown that copper reacts with N-acetyl-p-toluidine only in the presence of air to form an alcohol soluble compound which is apparently the true catalyst for the Ullmann reaction. An amount of this compound containing two milligrams of copper will catalyze the reaction of 0.05 mole of each of the reactants to a 35% yield.

"Naturkupfer C" gave no better yields than cuprous iodide or sheet copper for the reaction where no solvent was used. It was no better than copper reduced from the oxide or cuprous iodide when nitrobenzene was used as a solvent.

Phenol, copper and air form an active catalyst for the reaction of potassium phenoxide and phenyl bromide. The presence of phenol as a solvent is apparently necessary for this preparation.

It has not been found possible to substitute carbonates or bases for sodium or potassium carbonate or to use silver as a catalyst or to catalyze the reaction of phthalimide with phenyl or butyl bromide.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE INTERFERENCE OF NITRO AND AZO GROUPS ON THE ZEREWITINOFF METHOD FOR THE QUANTITATIVE ESTIMATION OF ACTIVE HYDROGEN

BY HENRY GILMAN AND ROBERT E. FOTHERGILL

RECEIVED NOVEMBER 22, 1927 PUBLISHED MARCH 7, 1928

Introduction

It has recently[1] been shown that nitro and nitroso groups interfere with the Zerewitinoff[2] method for the quantitative estimation of active hydrogen. The presence of such groups in a molecule is directly responsible for the liberation of very significant volumes of gas when the compound is treated with RMgX compounds having an alkyl group of low molecular weight.

Zerewitinoff[3] determined the number of active hydrogens in molecular compounds composed of substituted amines and trinitrobenzene, such as the trinitrobenzene complexes with *p*-amino-azobenzene and anthranilic acid. Each of these contains a primary amino group and it is known that one of the amino hydrogens reacts at room temperature and the second on heating. Zerewitinoff's results agree reasonably well on the basis of this general behavior, although there were more than the usual variations in quantity of gas evolved when the second hydrogen of primary amines is replaced. In view of our earlier work[1] it appeared that Zerewitinoff's results were incorrect, because the presence of trinitrobenzene in the complex molecule should have caused a larger evolution of gas than was reported by Zerewitinoff. We showed then that 1,3,5-trinitrobenzene evolved considerable gas when treated with ethylmagnesium bromide. This was contrary to the work of Ciusa[4] who reported that trinitrobenzene contained no active hydrogen.

There was the possibility that the nitro groups in the complexes studied by Zerewitinoff might have been so masked by the amino component that normal values would be obtained. However, the present work shows that such is not the case. The complexes give decidedly higher values for active hydrogen than those calculated for the amino group alone. The unavoidable conclusion is that the nitro groups are very largely responsible for the abnormal results.

We do not say that the nitro group is entirely responsible in every case for the higher values, because the complex formed from *p*-amino-azobenzene and trinitrobenzene contains, in addition to the amino and nitro

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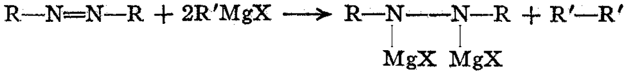
[1] Gilman and Fothergill, THIS JOURNAL, 49,2815 (1927).

[2] Zerewitinoff, *Ber.*, 40, 2023 (1907) and numerous succeeding papers. The most recent reference is *Z. anal. Chem.*, 68, 321–327 (1926); [*C. A.*, 21, 153 (1927)]. See also Chugaev, *Ber.*, 35,3912 (1902), for earlier experimental work on the same method.

[3] Zerewitinoff, *Ber.*, 43,3590 (1910).

[4] Ciusa, *Gazz. chim. ital.*, 50, II, 53 (1920) [C. *A.*, 15,837 (1921)].

groups, an azo group. Gilman and Pickens[5] have shown that the following reaction takes place between azo compounds and the Grignard reagent.



$$R{-}N{=}N{-}R + 2R'MgX \longrightarrow \underset{MgX}{R{-}N}{-}\underset{MgX}{N{-}R} + R'{-}R'$$

In view of this reaction it is to be expected that azo compounds under certain conditions should evolve gases when treated with RMgX compounds having an alkyl group of low molecular weight. A study of several typical azo compounds shows that an appreciable quantity of gas is evolved under the conditions used in our determination of active hydrogen by Zerewitinoff's method. Accordingly, the azo group is to be added to the nitro and nitroso groups as a group that interferes with the quantitative estimation of active hydrogen.

TABLE I

RESULTS

Compound	Compound, g.	Solvent for compound	No. of active hydrogens Room temp.	After warming to 70°
p-Amino-azobenzene-trinitrobenzene	0.2019	Xylene	2.17	3.46
	.1998	Xylene	1.88	3.18
	.2037[a]	Xylene	2.09	3.62
Anthranilic acid-trinitrobenzene	.0972	Xylene	2.50	3.54
	.0975	Xylene	2.51	3.47
Azobenzene	.2004	n-Butyl ether	.24	.29
p-Dimethylamino-azobenzene	.2049	n-Butyl ether	.33	.42
p-Amino-azobenzene	.2035	n-Butyl ether	1.69	2.18
	.2008	n-Butyl ether	2.14[b]	2.48[c]
Benzene-azodiphenylamine	.2012	n-Butyl ether	1.26	1.42 1.74[d]
Benzoic acid[e]	.2168	Xylene	1.03	1.15

[a] The methylmagnesium iodide used in this determination was prepared in iso-amyl ether, after the directions of Zerewitinoff.[8] However, Zerewitinoff found 1.03 active hydrogens at room temperature, and 2.02 active hydrogens after warming to 85° for five minutes.

[b] After standing at room temperature (31°) for fifteen hours.

[c] After warming to 50–70° for six hours.

[d] After warming to 70° and then standing for one and one-half hours at room temperature.

[e] This check experiment was carried out to determine the reliability of xylene as a solvent.

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[5] Gilman and Pickens, THIS JOURNAL, 47, 2406 (1925). The same mechanism, without proof, was offered earlier by Franzen and Deibel, *Ber.*, 38, 2716 (1905). However, their reaction with ethylmagnesium bromide is incorrect, inasmuch as present studies show that the gases evolved from azobenzene and ethylmagnesium bromide contain 25–30% of ethylene. The results of this disproportionation reaction between azobenzene and other RMgX compounds will be reported later.

Experimental

The apparatus and general technique was that described by Zerewitinoff,[2] except that n-butyl ether was used as the medium for methylmagnesium iodide in all but one of the determinations. Xylene was used in some of the analyses as a solvent for the complexes with trinitrobenzene because of their low solubility in n-butyl ether. In each determination the amount of gas evolved by the reaction at room temperature was first determined, and then the reaction mixture was heated to 70° for fifteen minutes, after which it was cooled to room temperature for the second value.

Summary

The complexes of *p*-amino-azobenzene and anthranilic acid with trinitrobenzene have been shown to give higher active hydrogen values than those reported by Zerewitinoff. These abnormal results are due to the interfering effect of the nitro and azo groups.

AMES, IOWA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE REACTION BETWEEN DUROQUINONE AND THE GRIGNARD REAGENTS[1]

BY LEE IRVIN SMITH AND H. MARJORIE CRAWFORD

RECEIVED NOVEMBER 25, 1927 PUBLISHED MARCH 7, 1928

Introduction and Historical Review. Statement of the Problem

In the first paper of this series[2] it was shown that the reaction between sodium malonic esters and duroquinone is not a simple addition reaction but is accompanied by oxidation leading to a product in which the malonic ester residue is linked by a double bond to what was originally one of the methyl groups of the quinone. This reaction involves the removal of both methylene hydrogen atoms of the malonic ester and both these hydrogen atoms are necessary in order for the reaction to take place.

In order to obtain more information concerning the addition of metallic derivatives to duroquinone, we have used in the present work a Grignard reagent. These reagents differ from sodium malonic ester in possessing no active "methylene" hydrogen atoms, and yet they have the advantage, in common with sodium malonic esters, of adding to carbonyl systems to give metallic derivatives which can be readily manipulated. By using the Grignard reagents we hoped to avoid the complicated oxidation reaction which accompanies the addition of sodium malonic ester and to

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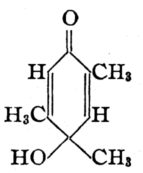
[1] Abstracted from a thesis by H. Marjorie Crawford, presented to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Smith and Dobrovolny, THIS JOURNAL, 48,1693 (1926).

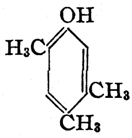
obtain products which would throw some light upon the mechanism of this malonic ester addition.

A review of the literature[3] shows that quinones may be divided into two classes: (a) quinones (such as anthraquinone) which can updergo only 1:2 addition at the carbonyl group. Only in this case is the reaction with a Grignard reagent a clean-cut one, and good yields of the mono- or di-addition product result depending upon the relative amounts of reagents used. (b) Quinones (such as *p*-xyloquinone and α-naphthoquinone) which can undergo 1:2, 1:4 or 1:6 addition, or a combination of them. In this case the reaction becomes quite complex and leads to a large number of products. Some of these products are solids, but the yield of crystallizable solids is always low and by far the largest amount of material turns up as tars and an uncrystalliiable oil, the nature of which no one, so far, has been able to determine.

The most thorough piece of work in this field is undoubtedly that of Bamberger and Blangey.[3g] Adding methylmagnesium iodide to *p*-xyloquinone, these investigators isolated from the reaction mixture six solid addition products, namely, pseudocumoquinol (A); its reduction product, pseudocumenol, (B); dihydrotrimethylquinone, (C); tetramethylcyclohexanedione, (D); prehnitol, (E) and p-dixyloquinol momomethyl ether, (F).



(A)



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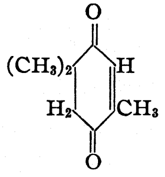

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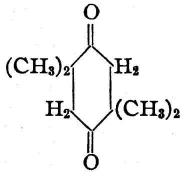

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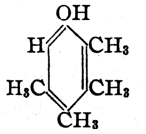
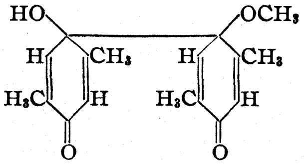


(E)



(F)

Of these six compounds, three (A, C, D) are the direct result of 1:2 or 1:4 additions to the conjugated systems in the quinone. Two others (B and E) are secondary products derived from direct addition products, while F is the only product whose formation could not have been predicted from a consideration of the addition reactions of conjugated systems

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[3] (a) Haller and Guyot, *Bull. soc. chim.*, 31,795 (1904); (b) Guyot and Staehling, *ibid.*, 33, 1104, 1144 (1905); (c) Clarke and Carleton, THIS JOURNAL, 33, 1966 (1911); (d) Werner and Grob, Ber., 37, 2887 (1904); (e) Bischoff, *Ber.*, 38, 2078 (1905); (f) Bamberger and Blangey, *Ber.*, 36,1625 (1903); (g) Ann., 384, 272 (1911); (h) Franssen, *Bull. soc. chim.*, 37,902 (1925).

alone. But the combined amount of these six products accounted for only one-fourth of the reagents used. Another fourth of the quinone was reduced to hydroquinone and the rest of the material turned up as amorphous material, tars and oils. Thus the reactions leading to the formation of these solid products were not the only ones taking place and there must have been several more occurring which were impossible to study. These results of Bamberger and Blangey are typical of all the published work in this field dealing with quinones in which the conjugated systems are open to attack by a Grignard reagent. In every such case the reaction gives more tars, oils and amorphous materials than anything else.

In the present work we have found that duroquinone, though a completely substituted quinone, gives the same sort of results that Bamberger and Blangey found xyloquinone produced. The yield of solid addition products is extremely low and by far the greater amount of the material turns up as an uncrystallizable oil, although we obtained no tars or amorphous material.

Choice of Grignard Reagent

Preliminary experiments with the reaction between duroquinone and Grignard reagents showed that large amounts of a yellow oil are produced. In order to determine whether or not the nature of the Grignard reagent was a factor in the production of this oil, we added the following to the quinone: methylmagnesium iodide, methylmagnesium bromide, ethylmagnesium bromide, phenylmagnesium bromide and α-naphthylmagnesium bromide. In every case large amounts of oil were formed and the amount of this oil is practically independent of the nature of the Grignard reagent. Because of this, our first detailed experiments were carried out using ethylmagnesium bromide, as this particular reagent was the easiest one for us to prepare in quantity.

Our next experiments were undertaken to determine quantitatively the amount of ethylmagnesium bromide which would react with a given quantity of duroquinone. Using a standard solution of the reagent and the procedure and apparatus of Gilman,[4] it was found that 1.6 moles of ethylmagnesium bromide react per mole of quinone but that a considerable amount of gaseous by-product results. This gas was collected and analyzed but the results of the analysis do not correspond with the calculated values for methane, ethane, ethylene or butane. About 10% of the gas is unsaturated (absorbed by concd. sulfuric acid or bromine water), and the remainder is a mixture of saturated hydrocarbons. We have assumed that this gas results from reactions of the Wurtz type and, since it is a rather complicated mixture and difficult to study, ethylmagnesium

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[4] Gilman and Crawford, THIS JOURNAL, 45,554 (1923).

bromide was discarded and phenylmagnesium bromide substituted for it. If the reactions producing the gaseous by-products are actually of the Wurtz type, then with phenylmagnesium bromide diphenyl and compounds related to it should result. These compounds are solids and the use of phenylmagnesium bromide in place of ethylmagnesium bromide should, if the two reagents behave in the same way, lead to by-products which would be easier to handle than the mixture of gases resulting when ethylmagnesium bromide is used. Our preliminary experiments justified these expectations; no gases are evolved when phenylmagnesium bromide is added to duroquinone and, therefore, we chose this particular Grignard reagent for the rest of our work.

Discussion of the Reaction

When duroquinone reacts with phenylmagnesium bromide, the yield and nature of the products, as well as the color changes taking place during the reaction, vary with the procedure and with the relative amounts of the two reagents used. When the Grignard reagent is added to the quinone, the color changes from yellow to orange to green as the metallic addition product is formed. When the reagents are added in the reverse order, the color becomes green at first, and then the solid addition product dissolves in the excess Grignard reagent, giving a yellow solution. Later, a heavy, yellow oil separates out below the ether layer. In either case the primary reaction product is a mixture of metallic derivatives which may be decomposed either by acids or by acetyl chloride. If acids are used for the decomposition, there results a mixture of hydroxyl compounds, practically all of which are "enols" and may rearrange partly or entirely into the corresponding keto forms. If acetyl chloride is used for the decomposition, the acetates of these hydroxyl compounds result. These acetates are stable and do not rearrange and, as they can be hydrolyzed later to give the hydroxyl compounds, the isolation, separation and purification of the reaction products is often greatly facilitated by using acetyl chloride instead of hydrochloric acid for the decomposition. The use of acetyl chloride for this purpose has the further great advantage of giving fewer compounds, for a pair of keto-enol isomers corresponds to only one metallic derivative and, consequently, to only one acetate. It is very interesting in this connection that benzoyl chloride and dimethyl sulfate are without effect upon these metallic derivatives—no benzoates or methyl ethers result and the magnesium derivatives remain unchanged after several hours' boiling with either of these reagents.

After decomposition of the metallic derivatives by hydrochloric acid or acetyl chloride the ether layer was separated, the aqueous layer extracted two or three times with ether and all the ether solutions were combined and evaporated to crystallization. After the solids were filtered off and the ether was fully evaporated from the mother liquor, there remained a dark, thick oil. This oil constitutes about 80% of the reaction product, the other 20% appearing as solid products. No amorphous substances were obtained and the amount of tarry material was very small.

Aside from hydroduroquinone and diphenyl, which are always formed, the solid addition products can be divided into two classes, as follows.

1. Mono-addition products, or their acetates, formed in accordance with the following equations (written as though C_6H_6 were added):

$$C_{10}H_{12}O_2 + C_6H_6 \longrightarrow C_{16}H_{18}O_2,\text{ or}$$
$$C_{10}H_{12}O_2 + C_6H_6 + CH_3COCl \longrightarrow C_{18}H_{20}O_3 + HCl$$

2. Di-addition products, or their di-acetates, formed in accordance with the following equations

$$C_{10}H_{12}O_2 + 2C_6H_6 \longrightarrow C_{22}H_{24}O_2,\text{ or}$$
$$C_{10}H_{12}O_2 + 2C_6H_6 + 2CH_3COCl \longrightarrow C_{26}H_{28}O_4 + 2HCl$$

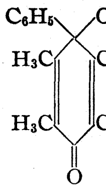
In general, when an excess of duroquinone is used, the mono-addition compounds are the chief products, while an excess of the Grignard reagent leads chiefly to the di-addition products. As mentioned above, the solid products constitute only 20% of the reaction mixture, the other 80% appearing as an oil. Since we were interested particularly in the solids, some preliminary experiments were conducted, varying the procedure and relative amounts of reagents in order to determine the best conditions for the production of solid material. In each experiment 10 g. of quinone was used and the result may be summed up briefly as follows. The largest amount of solid obtained in one run was 1.8 g. and the amount varied from this down to a mere trace. The largest amount of oil produced was 19.8 g. and in this case it was not accompanied by any solid material at all. The amount of quinone reacting varied from 0.9 to 10 g., that is, the amount of quinone recovered unchanged varied from 9.1 g. to zero. As a result of these experiments, we chose the following two procedures as giving the largest amounts of solid reaction products and the rest of our experiments were carried out according to one or the other of these procedures. Method (1): one equivalent of phenylmagnesium bromide was added to one equivalent of duroquinone, followed by decomposition of the metallic addition product by dilute hydrochloric acid. In this method the quinone is in excess until the end of the reaction and the solid products are chiefly mono-addition compounds. Method (2): one equivalent of duroquinone was added to four equivalents of phenylmagnesium bromide, followed by decomposition of the metallic addition products by acetyl chloride. In this method the Grignard reagent is in excess and the solid products are chiefly the di-addition compounds. In all our experiments we found the yields to be extremely variable, and two experiments, apparently conducted exactly alike, often gave different results. Because of this we always carried out our reactions with small amounts (10 to 20 g.) of duroquinone.

Discussion of the Reaction Products

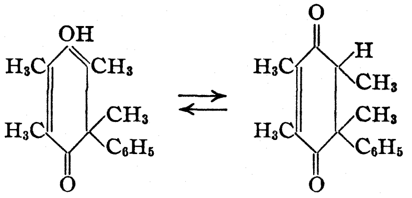
A. Compounds Formed by the Addition of One Molecule of Phenylmagnesium Bromide to One Molecule of Duroquinone.—When the reaction is carried out according to Method (1), the chief solid products are a yellow substance, m. p. 142°, and two white substances, m. p. 150 and 203°, all of which have the composition and molecular weight represented by the formula $C_{16}H_{18}O_2$. This composition corresponds to the addition of C_6H_6 to duroquinone

$$C_{10}H_{12}O_2 + C_6H_6 \longrightarrow C_{16}H_{18}O_2$$

It is possible to write three structural formulas corresponding to this composition which could result from the addition of one molecule of phenylmagnesium bromide to duroquinone, followed by hydrolysis. One of these (I) represents a 1:2 addition product and the other two represent the 1:4 addition product (IIA) and its keto form (IIB)



I (203°)



IIA (150°) IIB (142°)

The yellow compound, m. p. 142°, on oxidation with potassium permanganate in acetone gives acetophenone as one of the products. Since methyl and phenyl groups are attached to the same carbon atom in acetophenone, they must have been attached to the same carbon atom in the 142° compound, which eliminates structure I for this compound. When the 142° compound is ozonized, or oxidized very carefully by potassium permanganate, one of the products is a white acid having the composition $C_{12}H_{14}O_4$. If a substance with the structure represented by IIB were ozonized, one of the decomposition products to be expected would be α,β-dimethyl-α-phenyl succinic acid, $CH_3CH(COOH)C(CH_3)(C_6H_5)COOH$, $C_{12}H_{14}O_4$. A substance having the structure IIA, when ozonized, could not give any dibasic acid having the composition $C_{12}H_{14}O_4$, but would give the keto acid $CH_3COC(C_6H_5)(CH_3)COOH$, or its decomposition products, $CH_3COCH(CH_3)C_6H_5$ and $C_6H_5CH(CH_3)COOH$, none of which have the composition $C_{12}H_{14}O_4$. Structure IIR, then, correctly represents the yellow compound melting at 142°.

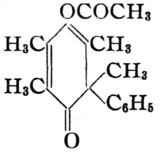
Both the 142' compound, (IIB), which is yellow, and the 150° compound, which is colorless, melt without decomposition to give yellow liquids. On cooling, these two substances solidify again, but when remelted the melting points show a drop until, after the fifth or sixth remelting, the two substances show approximately the same melting point (110°) and no longer solidify on cooling. This final melting point is practically the same as the melting point of a 1–1 mixture of the 142 and 150° compounds. The 203° compound shows no change in melting point after repeated melting and solidifying. This behavior indicates that the 142 and 150° compounds are the pair of keto-enol isomers IIA and IIB.

The 150° compound acetylates readily, giving a mono-acetate melting at 140°, and methylates easily to give a monomethyl derivative melting at 115°. All attempts to acetylate or methylate the 142° compound resulted in a yellow oil and unchanged material.

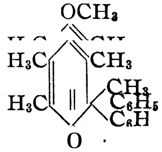
That the 150 and 142° mono-addition products as well as the 140° mono-acetate are closely related is shown by the following experiment, in which these three substances were all obtained from the same metallic derivative.

A reaction product obtained by adding one equivalent of phenylmagnesium bromide to 20 g. of duroquinone was divided into two parts. One part was decomposed with dilute hydrochloric acid and gave 0.45 g. of the 150° compound and 0.65 g. of the 142° compound. The other part was decomposed with acetyl chloride and gave 1.8 g. of the 140° mono-acetate. The amount of mono-acetate obtained corresponds to somewhat more than the combined amounts of the 150 and 142° compounds, but this may be accounted for by the fact that the acetates of these compounds are always more easily isolated from reaction mixtures than the unacetylated compounds. As is often the case, the 203° compound was not formed in this experiment. It never results in large amounts and the yield of it varies from zero to 2 g. per 50 g. of quinone.

These results indicate that the 150 and 142° mono-addition products are a pair of keto-enol isomers, and since the 142° compound has the structure IIB, the 150° compound must have the structure IIA. This leaves the structure I for the 203° mono-addition product, while the 140° mono-acetate has the structure III and the 115° methyl ether the structure IV



III



IV

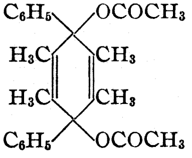
In several experiments according to method (1) there resulted small amounts of a red solid melting at 95°. This substance, in alcohol, gives a yellow solution of about the same intensity as duroquinone and on attempting to recrystallize it duroquinone was always found in the product. When steam distilled this red substance gives a distillate containing duroquinone and leaves a residue of the white compound, IIA. When equivalent amounts of the 150° compound, IIA, and duroquinone are dissolved in alcohol, the solution deposits red crystals, m. p. 95°, identical with those obtained from the original reaction mixture. This 95" compound is therefore a molecular compound of duroquinone and the 150° compound, IIA.

In one experiment according to method (1) a small amount of an orange compound, m. p. 135°, was obtained. This substance gives duroquinone on steam distillation but the residue is an oil. It has the same composition as the 95° molecular compound and is evidently another molecular compound of duroquinone and one of the mono-addition products, although we did not succeed in synthesizing it.

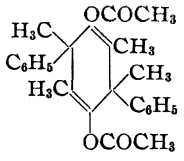
Method (1) also occasionally gives some dark green needles of the quinhydrone of duroquinone. It can be obtained by crystallizing a mixture of duroquinone and hydroduroquinone.

B. Compounds Formed by the Addition **of** Two Molecules of **Phenylmagnesium** Bromide **to** One Molecule **of Duroquinone.**—The chief **solid** products of reactions carried out according to method (2) are the 140° mono-acetate **III,** the diacetate of hydroduroquinone and a white compound melting at 245° and having the composition $C_{26}H_{28}O_4$. This composition corresponds to the addition of *2* molecules of C_6H_6 to one of duroquinone, followed by a double acetylation of the product, and its reactions show that the compound is a diacetate.

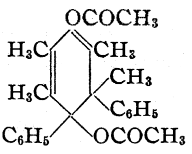
It is possible to write three structures which represent diacetates that could result from the addition of two molecules of phenylmagnesium bromide to one of duroquinone, followed by decomposition with acetyl chloride. These are V, in which both additions are 1:2 to carbonyl; VI in which both are 1:4 to the conjugated systems; and VII in which one addition is 1:2 and one 1:4.



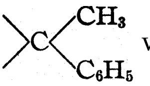
V



VI **(245")**

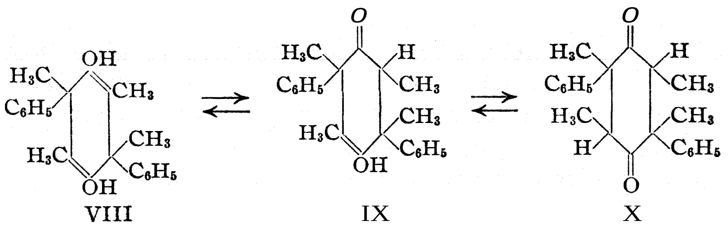


VII

The 142" mono-addition compound, IIB, reacts with phenylmagnesium bromide to give a metallic derivative which, when decomposed with acetyl chloride, gives the 245° diacetate and a dark oil. This eliminates structure V for that of the 245° diacetate, for the compound IIB has been shown to contain the grouping  which does not occur in V. Structure VII for this diacetate is eliminated as follows. A compound of this structure could result by **acetylating** either the product of 1:4

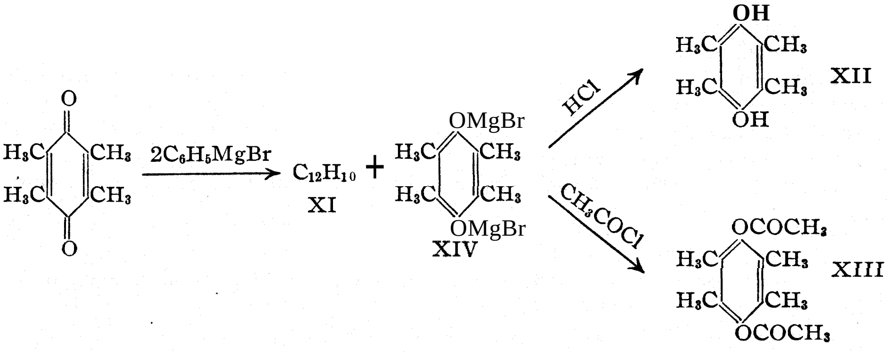
addition of phenylmagnesium bromide to I, or the product of a 1:2 addition of phenylmagnesium bromide to IIA or IIB; while VI cannot be obtained from the mono-addition products in any other way than by a 1:4 addition to IIA or IIB. The 203" compound, I, reacts with phenylmagnesium bromide, but the product on decomposition with either hydrochloric acid or acetyl chloride is a yellow oil and none of the very sparingly soluble 245° diacetate can be isolated from it. This leaves structure VI for the 245° diacetate.

When this diacetate is hydrolyzed, the products are solids which melt anywhere from 110 to 197°. None of the products of a fractional crystallization of these solids shows a constant melting point but all the fractions, no matter what the melting-point, give the same analyses and acetylate easily to give the 245° diacetate again. The composition of these solids is $C_{22}H_{24}O_2$, corresponding to the addition of $2C_6H_6$ to duroquinone. If the diacetate, VI, is hydrolyzed, the first product should be dihydroxyl compound VIII, which could isomerize to the two tautomeric forms IX and X.



The variable melting point of the solids obtained by hydrolyzing the diacetate is due to the establishment of equilibria between these three tautomers. All of them have the same composition and all three would, on acetylation, give the same diacetate.

C. By-products which Result, Regardless of Procedure.—Diphenyl, XI, and hydroduroquinone XII (or its diacetate, XIII, if the metallic derivatives are decomposed with acetyl chloride), are formed in small amounts in all reactions between the quinone and phenylmagnesium bromide and result from the reducing action of the Grignard reagent.



The three compounds XI, XII and XIII were all identified by comparison with known samples.

The thick, viscous oils, accounting for 75 to 80% of the reaction product, were obtained in all the reactions between the quinone and Grignard reagents, regardless of whether the metallic derivatives were decomposed with hydrochloric acid or acetyl chloride. This oil usually contains about 20% of quinone (and hydroquinone or its diacetate), which may be removed by adding $FeCl_3$-HCl to oxidize any hydroquinone and then distilling with steam, as the oil is only slowly volatile with steam. The residue from the steam distillation is a red oil only a small part of which (less than 10%) is alkali soluble. It cannot be distilled without considerable decomposition, even under reduced pressure, and shows no constant boiling point—thus, a sample of 34 g. gave 21 g. of distillate, b. p. 200–250° under 26 mm., and 10 g. of dark, tarry residue. We were not able to obtain any solid derivatives of this oil; it apparently does not react with dimethyl sulfate or acetyl chloride—at least the products are oils. It reduces potassium permanganate but the product is an oil which is not soluble in alkali and which gives only oils with phenylhydrazine. Bromination gives hydrobromic acid and a thick, red oil. Boiled with concd. nitric acid, it gives a yellowish semi-solid which gives only oils when attempts are made to recrystallize it.

No conclusions can be drawn regarding the nature of this oil other than to call attention to the fact that almost all of the solid products obtained in the reaction contain one or more asymmetric carbon atoms, and the oil may be a mixture of stereoisomers, as suggested by Kohler and Butler[5] in the case of oils which they obtained in some analogous reactions with the Grignard reagents and unsaturated carbonyl compounds.

Experimental Part[6]

Preparation and Purification of Reagents

Bromobenzene.—This was prepared by brominating benzene in the usual way. The product was fractionated twice, using a Glinsky column, and the fraction boiling at 150–154° under 738 mm. was considered pure enough for the purpose.

Magnesium.—This was a pure specimen, leaving almost no residue after reacting with bromobenzene.

Ether.—This was purified by shaking with water to remove alcohol and then with potassium permanganate. After standing over calcium chloride for a week, and then over phosphorus pentoxide for a day, it was distilled directly from the phosphorus pentoxide and kept over sodium wire.

Duroquinone.—This was made by the method described by Smith and Dobrovolny.[7]

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[5] Kohler and Butler, This Journal, 48, 1047 (1926).

[6] The carbon-hydrogen analyses were carried out by the semi-micro method developed in this Laboratory by W. M. Lauer.

[7] Smith and Dobrovolny, This Journal, 48,1420 (1926).

Details of Procedure

Method (I).—One-tenth of a mole of phenylmagnesium bromide in ether was added, through a dropping funnel, to an ether solution of 10 g. of duroquinone (0.061 mole) in a liter round-bottomed flask fitted with a reflux condenser and a calcium chloride guard tube. The flask was shaken frequently during the addition and the metallic addition product deposited as a bright yellowish green solid. The reaction mixture, after standing overnight, was decomposed with iced hydrochloric acid. The layers were separated, the water layer was extracted several times with ether, all the ether solutions were combined, dried over calcium chloride and then evaporated to about 40 cc. Solid material was deposited on cooling. This was filtered off and recrystallized. It was the 142° mono addition compound, IIB. Five runs, each of 10 g. of duroquinone, gave 1.6, 2.7, 2.1, 2.0 and 3.4 g., an average of 2.3 g. per 10 g. of quinone. The oily residues from these runs were combined and, after standing for several days, it deposited a small amount of the 203° compound I. Later, a small amount of the 95° red molecular compound crystallized out and there remained 73 g. of oil which, on steam distillation, gave some duroquinone and diphenyl. The 203° compound I was usually mixed with the 142° compound IIB, and since their solubilities are so nearly the same, the only means of separation was to pick out the two different kinds of crystals (white and yellow) with a small pair of tweezers under a large lens; yield from 50 g. of duroquinone: 11.8 g. of 142° compound IIB, 2.0 g. of 203° compound I, small amount of 95° molecular compound, 73 g. of oil. It is not possible, however, to give much more than a general idea as to yields of the various products for the yields vary widely, even when apparently identical procedures are used.

Method (2).—Phenylmagnesium bromide was prepared from 38.3 g. of bromobenzene and 5.85 g. of magnesium. After the reaction was completed, the ethereal solution of phenylmagnesium bromide was poured into a dry, liter round-bottomed flask fitted with reflux condenser and dropping funnel. A solution of 10 g. of duroquinone in ether was slowly added from the dropping funnel, with frequent shaking. The reaction product was a green solid which dissolved in the excess of phenylmagnesium bromide to give a yellow solution. After about three-fourths of the quinone had been added, a heavy yellow oil settled out below the ether. When the quinone was all added, the reaction mixture was allowed to stand for several hours and was then decomposed by adding 21 g. of acetyl chloride through the dropping funnel. This amount of acetyl chloride is a slight excess calculated on the phenylmagnesium bromide used. The solution was heated on the steam-bath for half an hour and then water was added to decompose the excess acetyl chloride. The layers were separated, the water layer was extracted several times with ether and all the ether solutions were combined. Any solid material (the diacetate VI) suspended in the ether was filtered off, the filtrate dried over calcium chloride and evaporated to about 75 cc. The diacetate VI crystallized on cooling. This was filtered off and the filtrate allowed to concentrate by evaporation, when the diacetate of hydroduroquinone, m. p. 202° (XIII), appeared. On longer standing the filtrate deposited the 140° mono-acetate (III) and a dark viscous oil remained; yield from 10 g. of quinone, 2.35 g. of 245° diacetate (VI), 1.3 g. of 202° diacetate of hydroduroquinone (XIII), 0.75 g. of 140° monoacetate (III) and 23 g. of oil. If the reaction product is steam distilled immediately after the decomposition with acetyl chloride diphenyl may be isolated from the distillate. The residue from the steam distillation is then extracted with ether and the separation of solids carried out as before.

Properties and Reactions of the Individual Solid Products

2,3,5,6-Tetramethyl-1-phenylcyclohexadiene-2,5-one-4-ol-1 (I) crystallizes from alcohol or ether in hard, colorless, transparent prisms, m. p. 203°. It does not form a semicarbazone or phenylhydrazone, gives a yellow oil on acetylation and is recovered unchanged on treatment with dimethyl sulfate. Oxidation with potassium permanganate gives a yellow oil which is not soluble in sodium bicarbonate. It reacts with phenylmagnesium bromide to give a metallic derivative, but on acidification an oil results, along with diphenyl.

Anal. Calcd. for $C_{16}H_{18}O_2$ (242): C, 79.3, H, 7.5. Found: C, 79.2, 79.6, 79.4, 79.1; H, 7.4, 7.3, 7.7, 7.6.

Mol. wt. Subs., 0.1506, 0.1506; benzene, 13.88, 19.97. AT, 0.185°, 0.132°; mol. wt., 293,285.

2,3,5,6-Tetramethyl-3-phenylcyclohexadiene-1,5-one-4-ol-1 (IIA) crystallizes from alcohol in colorless, square, transparent plates, m. p. 150°. It does not react with phenylmagnesium bromide. Oxidation with potassium permanganate gives an oil partly soluble in sodium carbonate. It acetylates easily and methylates with dimethyl sulfate and alkali. It forms a red molecular compound with duroquinone.

Anal. Calcd. for $C_{16}H_{18}O_2$ (242): C, 79.3, H, 7.5. Found: C, 79.5, 78.9, 79.2; H, 7.4, 7.4, 7.4.

Mol. wt. Subs., 0.0857, 0.0857; benzene, 15.385, 27.73. *AT,* 0.105°, 0.063"; mol. wt., 264, 245.

Derivatives.—Acetate (III), white needles, m. p. 140°, extremely soluble in alcohol and ether. Does not decolorize potassium permanganate on standing for 24 hours. Does not react with phenylmagnesium bromide. Requires alcoholic potash or sodium ethylate for hydrolysis, and the product is the parent compound, IIA.

Anal. Calcd. for $C_{18}H_{20}O_3$ (284): C, 76.0, H, 7.1; Found: C, 76.0, 75.8, 75.9; H, 7.1, 7.1, 7.2.

Mol. wt. Subs., 0.3000, 0.3000; bromoform, 40.024, 65.58. *AT,* 0.380°, 0.233'; mol. wt., 284,283.

METHYL ETHER (IV) crystallizes in long, white needles from methyl alcohol; m. p. 115". Is not oxidized by potassium permanganate.

Anal. Calcd. for $C_{17}H_{20}O_2$ (256): C, 79.6, H, 7.9. Found: C, 79.4, H, 8.7.

MOLECULAR COMPOUND WITH DUROQUINONE.—Crystallizes from alcohol, in which it is quite soluble, in bright red prisms, m. p. 95". The alcoholic solution has the pale yellow color of duroquinone.

Anal. Calcd. for $C_{10}H_{12}O_2 + C_{16}H_{18}O_2 = C_{26}H_{30}O_4$: C, 76.8, H 7.4. Found: C, 76.5, 77.7; H, 7.2, 7.4.

Mol. wt. Subs., 0.1511, 0.1511; benzene, 15.07, 20.57. *AT,* 0.258°, 0.181°; mol. wt., 194,203. Calcd. for $^1/_2$ $(C_{10}H_{12}O_2 + C_{16}H_{18}O_2)$, 203.

2,3,5,6-Tetramethyl-3-phenylcyclohexene-5-dione-1,4 (IIB) is quite soluble in alcohol and ether, from which it crystallizes in hard, transparent, yellow hexagons, m. p., 142°. It reacts with phenylmagnesium bromide to give a metallic derivative which, decomposed with acetyl chloride, gives the 245° diacetate VI. Does not react with phenylhydrazine or hydroxylamine, and with semicarbazide gives an isomeric compound, m. p. 62°, which contains no nitrogen. Acetylation gives a yellow oil and unchanged material. Methylation with dimethyl sulfate and alkali gives an oil and unchanged material, but attempted methylation with methyl iodide and sodium methylate gives the same isomeric compound, m. p. 62°, that is obtained when attempts are made to form a semicarbazone. Bromination gives a yellow oil.

Anal. Calcd. for $C_{16}H_{18}O_2$ (242): C, 79.3, H, 7.5. Found: C, 79.4, 78.8; H, 7.4, 7.4.

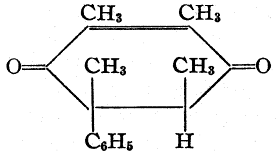
Mol. wt. Subs., 0.1506, 0.1500; benzene, 14.21, 13.26. AT, 0.224°, 0.232"; mol. wt., 237, 244.

OXIDATION.—One g. of the solid was dissolved in 50 cc. of acetone, the solution cooled and powdered potassium permanganate added as long as any decolorization took place (about 1.7 g. of potassium permanganate). The solution became brown at once but no manganese dioxide precipitated until about 1 g. of potassium permanganate had been added. The solution was then warmed to room temperature, when a little more potassium permanganate reacted, after which it was poured onto iced sulfuric acid and decolorized with sodium bisulfite. The solution was extracted with ether and the aqueous layer discarded. The ether layer was extracted with sodium bicarbonate. and the bicarbonate solution, on acidification, gave a precipitate of a white acid; m. p. 170–172°. The ether layer was evaporated and the residue (oil), when treated with semicarbazide, gave the semicarbazone of acetophenone. Ozonization in carbon tetrachloride gives a viscous oil from which the same acid, m. p. 170–172°, can be extracted with sodium bicarbonate, but no acetophenone results. This acid is slightly soluble in cold water but dissolves in boiling water, from which it crystallizes slowly on cooling. It is difficultly soluble in benzene but very soluble in ether.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.4. Found: C, 65.6, 65.2; H, 6.6, 6.8.

Eq. wt. Subs., 0.1568; NaOH (0.1188 N) 11.8 cc. = 0.0560 g. of NaOH. Eq. wt., 112. The simplest formula which will satisfy both the analysis and equiv. wt. determination and which contains a phenyl group is $C_{12}H_{14}O_4$, mol. wt. 224, and from its method of formation, and the fact that acetophenone usually accompanies it, we regard this acid as α,β-dimethyl-α-phenyl succinic acid, $CH_3CH(COOH)C(CH_3)(COOH)C_6H_5$. Several attempts were made to synthesize this substance, but none of them was successful.

As mentioned above, when the compound IIB is treated with semicarbazide, or with methyl iodide and alkali, it gives a pale yellow, isomeric substance; m. p. 62°. So little of this material was available that no extensive investigation of it could be made. When fused and inoculated with a crystal of the 142° compound IIB, the substance undergoes no change. We are inclined to regard it as a geometric isomer of the 142° compound, which is the only mono-addition compound capable of existing in two geometric forms.



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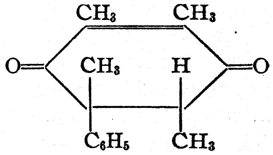


Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.5. Found: C, 78.4, 79.7; H, 7.9, 7.8.

Molecular compound, $C_{16}H_{18}O_2$ + duroquinone.—About 0.2 g. of an orange compound, m. p., 135°, was obtained once in a reaction carried out according to method (1). It is soluble in alcohol, from which it crystallizes in orange plates. On standing this orange compound turns yellow. Distillation with steam gives duroquinone and leaves a residue of oil which apparently contains no solid material.

Anal. Calcd. for $C_{16}H_{18}O_2 + C_{10}H_{12}O_2$: C, 76.8; H, 7.4. Found: C, 76.7, 77.3; H, 7.5, 7.6.

The compound is apparently a molecular compound of duroquinone and one of the mono-addition products, but we were not able to synthesize it by crystallizing together duroquinone and any of the mono-addition products.

Di-addition Compounds, $C_{22}H_{24}O_2$ (VIII, IX or X).—The di addition product is best obtained by isolating it from the reaction product as the diacetate and then hydrolyzing. It is a white solid, very soluble in alcohol or ether, from which it recrystallizes in fairly large needles. The melting point varies with the procedure and recrystallization of the various fractions does not lead to any definite separation. The melting points of the products we obtained varied from **115** to **197°.** All of these products gave the same analyses and acetylated easily to give the same diacetate. The substance is very stable—it does not reduce potassium permanganate, and it merely acetylates when boiled with chromic acid in glacial acetic acid. It does not react with semicarbazide. All attempts to methylate it, using dimethyl sulfate and alkali, gave unchanged starting material. It reacts with bromine in carbon tetrachloride to give hydrobromic acid and a white, monobromo compound; m. p. **163–164°.** ***Anal.*** Calcd. for $C_{22}H_{23}O_2Br$: Br, **20.0.** Found: Br, **20.9.**

Anal. Calcd. for $C_{22}H_{24}O_2$: C, **82.5;** H, **7.6.** Found (a) sample, m. p. 184°, direct from Grignard reaction: C, **81.1, 81.6;** H, **7.3, 7.4;** (b) sample, m. p. **144°,** from hydrolysis of the diacetate: C, 82.2, 81.7; H, 7.8, 7.3; (c) sample, m. p. **197°,** from hydrolysis of the diacetate: C, **82.1, 81.9;** H, **7.2, 7.6;** (d) sample, m. p. **115°,** from hydrolysis of the diacetate: C, 79.8, 81.4; H, 7.5, 7.8.

Mol. wt. Subs.; **0.1505, 0.1505;** benzene, **14.94, 20.27.** AT, 0.163°, **0.121°;** mol. wt., **308.307.** Calcd. for $C_{22}H_{24}O_2$, **320.**

The substance acetylates easily and quantitatively when its solution in acetic anhydride is treated with a drop of concd. sulfuric acid and warmed for an hour. Because of this easy acetylation we have written the structure chiefly as the diol VIII, but the melting points of the different samples indicate that it is a mixture.

2,3,5,6-Tetramethyl-3,6-diphenylcyclohexadiene-1,4-diol-1,4-diacetate (VI).—This substance is obtained by acetylating any of the di-addition products, or it may be obtained directly from the product of the Grignard reaction according to method **(2)** by decomposing the metallic derivatives with acetyl chloride. It is only slightly soluble in alcohol, ether and benzene but quite soluble in chloroform, bromoform and carbon tetrachloride. It crystallizes from a mixture of chloroform and ethyl alcohol in small, white prisms; m. p. **245°.** It is extremely stable and is not affected by potassium permanganate, chromic acid or ozone. It can be hydrolyzed by 60% sulfuric acid, but better results are obtained if it is refluxed with sodium ethylate. Five g. refluxed with a solution of **2** g. of sodium in **100** cc. of 95% ethyl alcohol for ten hours, followed by standing overnight, gave **2.04** g. of solid, m. p. 165°, and the filtrate diluted with water, acidified and then extracted with ether gave, as the ether evaporated, the following solids: **0.289** g., m. p. **155";** **0.025** g., m. p. 140°; **0.659** g., m. p. **133";** **0.228 g.,** m. **p. 115";** **0.040 g., m.** p. 110–117° and a small amount of yellow oil. Total solids, **3.28** g Theory from **5** g. of diacetate, **3.96** g. All of these solids acetylated easily to give the same diacetate.

Anal. Calcd. for $C_{26}H_{28}O_4$: C, **77.2,** H, **7.0.** Found: C, **76.4, 76.6, 76.4; H,** 6 9, **6.9, 6.8.**

Mol. wt. Subs., **0.3000, 0.2000, 0.2000;** bromoform, **62.33, 56.01, 84.83.** AT, 0.180°, 0.133°, **0.087";** mol. wt., **385,387, 390.** Calcd. for $C_{26}H_{28}O_4$: **404.**

All the other solid products obtained were known and were identified by their mixed melting points with prepared specimens. These compounds were: diphenyl, m. p. 69°; hydrodmoquinone, m. p. **230";** and hydroduroquinone diacetate, m. p **202°.** One new derivative of hydroduroquinone was made in the course of the work, namely, the dibenzoate. Two equivalents of phenylmagnesium bromide was added to one equivalent of hydroduroquinone suspended in ether. A bright robin's egg blue color developed. After the reaction was complete, an excess of benzoyl chloride was added. The solution became yellow and a white solid settled out. Recrystallized from a mixture of chloroform and ethyl alcohol, it melted at **259–260°.** It was very difficult to burn completely in the combustion apparatus.

Anal. Calcd. for $C_{24}H_{22}O_4$: C, 77.0; H, 5.9. Found: C, 76.9, 76.5; H, 6.7, 6.3.

No oily by-products were obtained in this reaction, and none result when the diacetate of hydroduroquinone is made in the same way. Hence the oils obtained when the quinone reacts with the Grignard reagent are not formed from the hydroquinone. But the blue color which develops when phenylmagnesium bromide is added to hydroduroquinone may, with the yellow of the quinone, be the cause of the green color which always appears as the reaction between duroquinone and phenylmagnesium bromide takes place.

Summary and Conclusions

1. Several Grignard reagents have been added to duroquinone.
2. With phenylmagnesium bromide, twelve solids were isolated from the reaction mixture. Four of these were already known and the other eight have been described in this paper, together with three other new compounds which were not obtained directly from the reaction mixture.
3. In so far as a quinone is comparable to an α-β unsaturated ketone, the solid products of the reaction are those which would be expected.
4. Compounds were formed by a reaction involving the 1:6 system in the quinone, but two molecules of Grignard reagent were necessary and this reaction cannot be considered a 1:6 addition in the usual sense.
5. There is no evident relationship between the results of this work and those obtained by Smith and Dobrovolny on the addition of sodium malonic esters to duroquinone. This lack of relationship between the two pieces of work supports the interpretation already given for the malonic ester reaction: namely, that it is an oxidation in the presence of alkali, which could not occur in the work with the Grignard reagent.
6. About 80% of the reaction product between duroquinone and any Grignard reagent is an oil which may be a mixture of stereoisomers This oil cannot be crystallized nor can it be distilled undecomposed.

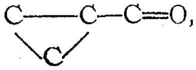
MINNEAPOLIS, MINNESOTA

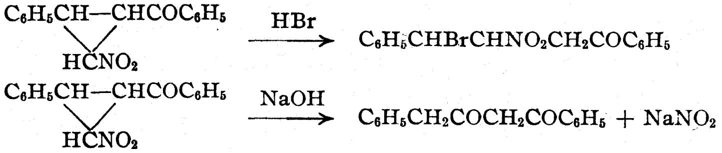
[Contribution from the Chemical Laboratory of Harvard University]

STUDIES IN THE CYCLOPROPANE SERIES. XI. CYCLOPROPANE DERIVATIVES WITH A TERTIARY NITRO GROUP ATTACHED TO THE RING

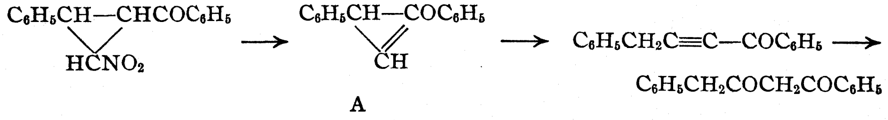
By E. P. Kohler and Paul Allen, Jr.

Received December 1, 1927 Published March 7, 1928

In earlier papers dealing with the characteristics of the unsaturated system , it was shown that most of the compounds containing this complex behave essentially like those containing the conjugated system C=C—C=O. The only notable exception to this rule occurs in the case of those nitrocyclopropane derivatives in which a nitro group is attached to the ring. Even these combine with acids in a normal manner, but the products formed by bases do not appear to be the result of a process that starts with addition.[1]



The evidence accumulated by a study of a number of such nitrocyclopropane derivatives[2] led to the conclusion that the first step in the reaction with bases is elimination of nitrous acid, and that the final product of the reaction is due to the instability of the resulting cyclopropene derivative. The probable mechanism of the reaction was, therefore, represented as follows



This mechanism is in complete accord with the general experience that bases tend to transform unsaturated compounds into more acidic forms. At the time it was proposed it was also consistent with all that was known about the behavior of cyclopropene derivatives, because the few that had been studied are so constituted that they are incapable of rearrangement into acetylenic compounds. Since then, however, Farmer and Ingold[3] have made cyclopropene dicarbonic acid—B or C—and have found that boiling alkalies transform it into a-ketoglutaric acid.

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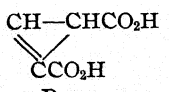
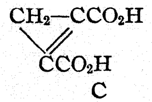
[1] Kohler and Engelbrecht, This Journal, 41, 1379 (1919).

[2] (a) Kohler and Williams, *ibid.*, 41, 1644 (1919); (b) Kohler and Srinivasa Rao, *ibid.*, 41, 1697 (1919); (c) Kohler and Smith, *ibid.*, 44,624 (1922).

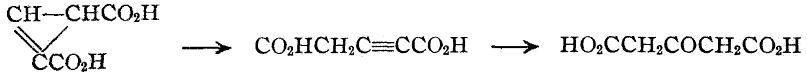
[3] Farmer and Ingold, *J. Chem. Soc.*, 119,2015 (1921).


B

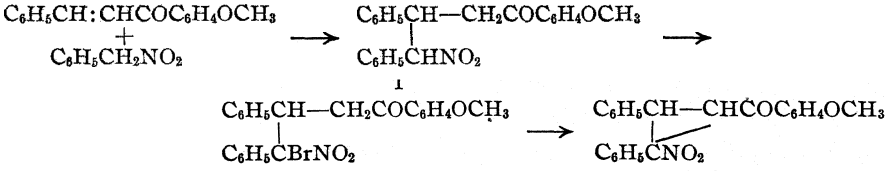

C

$HO_2CCH_2CH_2COCO_2H$

In accordance with the mechanism proposed for the nitro compounds, this cyclopropene acid could undergo rearrangement to an acetylenic derivative, but this would of necessity be the acid D which he expected to give acetone dicarbonic acid in place of the ketoglutaric acid that was actually obtained.


D

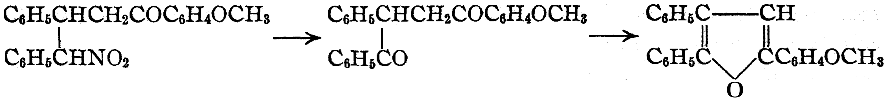
Even though these new facts are not necessarily inconsistent with the proposed mechanism—because the cyclopropene acid has possibilities of conjugation that are lacking in A—it nevertheless seemed advisable to test this mechanism further by studying the action of bases on a nitro-cyclopropane derivative so constituted that it might lose nitrous acid but could not form an acetylenic compound. To this end we undertook the preparation of 1-nitro-1,2-diphenyl-3-anisoyl cylopropane by the following steps


I

II

III

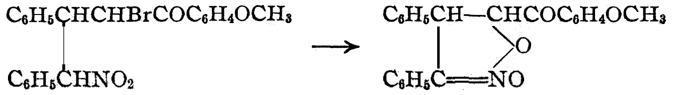
The addition of phenylnitromethane to the unsaturated ketone was accomplished with comparative ease, and the structure of the addition product was established by hydrolysis to a diketone which was readily condensed to a furane derivative a characteristic property of γ-diketones.


I

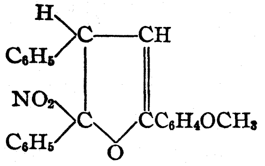
IV

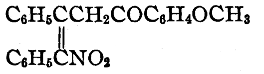
V

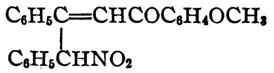
Direct bromination of the addition product yielded two isomeric α-bromo derivatives which proved to be useless for our purpose because, unlike the corresponding derivatives of the nitromethane addition product, they formed only isoxazoline oxides when treated with reagents capable of eliminating hydrogen bromide.

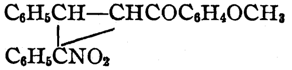


Indirect bromination of the addition product, by way of its sodium salt, gave the γ-bromo derivative II. This served our purpose, but the elimination of hydrogen bromide was troublesome. Even under the most favorable conditions—prolonged digestion with methyl alcoholic potassium acetate—it resulted in a mixture containing the addition product I, the diketone IV, variable quantities of uncrystallizable oils and two substances formed by elimination of hydrogen bromide. By derivation these two substances might be dihydrofurane derivatives, ethylenic compounds or the desired cyclopropane derivatives; but since neither of them forms an ozonide, they must be two of the four possible stereoisomeric cyclopropane derivatives represented by III.



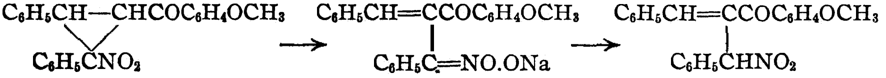

$\underset{\overset{\|}{C_6H_5CNO_2}}{C_6H_5CCH_2COC_6H_4OCH_3}$


$\underset{\overset{|}{C_6H_5CHNO_2}}{C_6H_5C{=}CHCOC_6H_4OCH_3}$



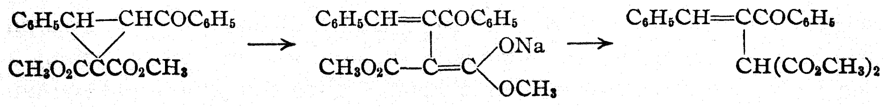
III

These cyclopropane derivatives react very readily with strong bases, and, fortunately, in view of the difficulty of securing the materials, the reactions are quite definite. Cold concentrated sodium methylate converts the higher-melting isomer quantitatively into a sodium compound that crystallizes in thick, yellow needles. This sodium compound, when acidified with due caution, yields two colorless products, of which one regenerates the same sodium compound when it is treated with sodium methylate, while the other forms a sodium compound that crystallizes in yellow prisms. The two colorless products are isomeric with each other as well as with the cyclopropane derivative from which they are formed. Each of them reduces permanganate and each also forms an ozonide which, when decomposed with water, yields benzaldehyde as one of the products. These substances are, therefore, stereoisomeric ethylenic compounds formed by opening the cyclopropane ring without eliminating the nitro group

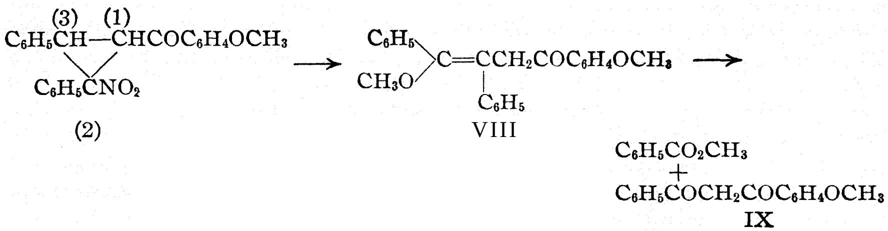


III VI VII

Evidently the mechanism of the reaction between bases and this tertiary nitro compound is totally different from that of the corresponding reaction with cyclopropane derivatives containing a secondary nitro group; the ring is opened at a different point and the product is a nitro compound which is stable toward bases. Indeed the behavior of this cyclopropane derivative is precisely the same as that of the dicarboxylic esters described and discussed in the first paper of this series.



The lower-melting cyclopropane derivative dissolves rapidly in sodium methylate without producing more than a trace of color and the solution promptly begins to deposit a colorless solid which contains neither nitrogen nor sodium. This product does not reduce permanganate but it combines with ozone, and when the resulting ozonide is decomposed with water it yields methyl benzoate and benzoyl-anisoyl-methane



IX

As not infrequently happens in studies of the mechanism of reactions, these results start more problems than they solve. Inasmuch as they show that β-diketones are not formed from those cyclopropane derivatives which are incapable of yielding acetylenic ketones, they bring a measure of support to the mechanism under investigation; but since we failed to secure any indication of the intermediate formation of cyclopropene derivatives, the evidence in favor of that mechanism is still far from conclusive.

A comparison of the products obtained from the two stereoisomers shows that the action of alkalies on nitrocyclopropane derivatives depends to a surprising degree upon their configuration. In order to obtain the ethylenic compound VII from the higher-melting isomer it is necessary to open the ring between carbon atoms (2) and (3); the ethylenic compound VIII from the lower-melting isomer cannot be formed by opening the ring at this point. From the behavior of unsaturated compounds containing conjugated systems it might be anticipated that these stereoisomers would neither add bases nor lose nitrous acid with the same ease, and that consequently the three-membered ring would be opened more readily in one of the isomers than in the other. But nothing in the chemistry of either cyclic or unsaturated compounds would lead to the expectation that in these stereoisomers the ring would be opened at different points by the same reagent.

Experimental Part

I. The Saturated Compounds

Phenylnitromethane cannot be added quite as easily or as completely to benzal acetyl anisole as to benzalacetophenone, mainly because the former is only moderately soluble in boiling methyl alcohol. For this reason it is best to prepare a small sample of the addition product by boiling a solution of equivalent quantities of ketone, nitro compound and sodium methylate in the requisite quantity of methyl alcohol. Once a sample is available for inoculation, it is possible to add in the presence of a much smaller proportion of the methylate and thereby increase the yield as well as simplify the isolation of the addition product. The procedure then is as follows.

To a solution of the unsaturated ketone in six times its weight of boiling, anhydrous, methyl alcohol are added in succession an equivalent quantity of the nitro compound and enough concentrated sodium methylate solution to produce decided alkalinity. The resulting mixture is boiled for half an hour, then inoculated with a sample of the addition product. This usually starts crystallization throughout the liquid but it is sometimes necessary to heat for a longer period before the mixture can be successfully inoculated. Even after crystallization has begun the mixture is kept boiling vigorously until it becomes so nearly solid as to render this impossible. It is then cooled and filtered. The solid is washed with boiling methyl alcohol until colorless. Filtrate and washings are combined, made decidedly alkaline with sodium methylate and slowly concentrated by distillation. In one operation 120 g. of ketonic and 70 g. of the nitro compound in 750 cc. of methyl alcohol gave, after two hours, 153 g. of almost pure addition product, and an additional 18 g. of somewhat less pure substance was obtained from the filtrate, making a total yield of 171 g. or 90%. Recrystallization from chloroform reduced this to 86%.

α-Anisoyl-β,γ-diphenyl-γ-nitro Propane, I.—The addition product is sparingly soluble in all common solvents except boiling glacial acetic acid. Relatively pure material is purified further by crystallization from chloroform, less pure material by crystallizing first from glacial acetic acid. The substance crystallizes in thin, feathery, white needles and melts at 164–165°.

Anal. Calcd. for $C_{23}H_{21}O_4N$: C, 73.6; H, 5.6. Found: C. 73.2; H, 5.6.

α-Anisoyl-β-phenyl-β-benzoyl Ethane, IV.—The addition product can be recrystallized from methyl alcoholic hydrochloric acid without loss, and it can also be dissolved in sodium methylate solution and, without loss, recovered by addition of acetic acid, but if the methylate is acidified with hydrochloric acid most of the substance is hydrolyzed to the diketone. This separates in well-formed, colorless prisms. It is readily soluble in chloroform, hot benzene and boiling methyl alcohol, sparingly soluble in ether, and it melts at 155–156°.

Anal. Calcd. for $C_{23}H_{20}O_3$: C, 80.2; H, 5.8. Found: C, 80.9; H, 5.9.

The **dioxime** was obtained by boiling the ketone for two and one-half hours with excess of **hydroxylamine** and potassium hydroxide in methyl alcohol. It crystallizes from aqueous methyl alcohol in colorless prisms melting at 180–181°.

Anal. Calcd. for $C_{23}H_{22}O_3N_2$: C, 73.8; H, 5.9. Found: C, 73.6; H, 6.1.

2,3-Diphenyl-5-(*p*-methoxyphenyl) Furane, V.—A solution of 1.4 g. of the finely powdered diketone in 25 cc. of cold concentrated sulfuric acid was left to itself for several hours, then poured onto cracked ice. In the course of an hour the deep red solution changed into a pasty solid which was purified by recrystallization from methyl alcohol. It separated in bunches of fine, white needles melting at 94–95'; yield, 75.5%.

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.7; H, 5.5. Found: C, 84.6; H, 5.6.

α-Anisoyl-β,γ-diphenyl-γ-nitro-γ-bromo Propane, II.—A solution of 190 g. of the crude washed and dried addition product in the minimum quantity of 30% sodium methylate solution was cleared by filtration, then cooled in ice water. The cooled solution was shaken vigorously while bromine was added drop by drop until the color was no longer discharged—about 90 g. The mixture was then stirred into water containing a little bisulfite. This dissolved the sodium bromide which separated during the reaction and precipitated the bromo compound as a pale yellow solid. After thorough washing and drying the bromo compound was recrystallized from chloroform and methyl alcohol. This gave 212 g. of pure product—a yield of 92%. The bromo compound is always contaminated with a small quantity of the dibromide of benzal acetyl anisole, which can be removed only by repeated recrystallization from methyl alcohol. It, therefore, generally melts at 135–139° while the perfectly pure substance melts at 140°. It crystallizes in colorless plates or tables.

Anal. Calcd. for $C_{23}H_{20}O_4NBr$: C, 60.8; H, 4.4. Found: C, 60.2; H, 4.5.

II. The Cyclopropane Derivatives

The preparation of the cyclopropane derivatives from the bromo compound is troublesome for various reasons. One is that the γ-bromo compound is easily reduced to the saturated nitro compound and this is gradually hydrolyzed to the diketone by potassium acetate and acetic acid. This difficulty can be avoided in part by using dilute solutions of strong bases but these more or less rapidly destroy the cyclopropane derivatives. We tried alcoholic sodium hydroxide, alcoholates, organic bases and solutions of potassium acetate in various alcohols. In the end we decided that methyl alcoholic potassium acetate was the most serviceable, hence only the results obtained with this reagent will be described. Our procedure was as follows.

A suspension of equal weights of powdered bromo compound and potassium acetate in 5 times their combined weight of methyl alcohol is boiled for twenty-four hours, then set aside for six to eight hours. The liquid soon turns yellow and all of the bromo compound usually is in solution after six to seven hours. The solution generally still contains some bromo compound after twenty-four hours but the yield of cyclopropane derivatives is less if the heating is more prolonged. On cooling, the clear solution gradually deposits a solid which is composed almost entirely of the higher-melting cyclopropane derivative and the reduction product, and which is separated without great difficulty by means of methyl alcohol. If the solution is set aside for a longer period it deposits also unchanged bromo compound, diketone, and at times, also, the lower-melting cyclopropane derivative—a mixture extremely difficult to separate.

The filtrate from the less soluble products is distilled until most of the methyl alcohol is gone, then poured into a large quantity of water, which precipitates a yellow oil or a pasty solid. Ether is added, the mixture is shaken vigorously for some time, then set aside for several hours. The resulting solid, when washed with ether until it is free from color, is composed almost entirely of the lower-melting cyclopropane derivative and the reduction product; it is separated without any great difficulty by recrystallization from methyl alcohol. When the ether-water mixture is allowed to stand for longer periods, the solid contains also unchanged bromo compound and diketone, and then is extremely difficult to separate. The ethereal layer contains unchanged bromo compound and all of the products, including a large quantity of yellow oil; its separation is unremunerative. In one experiment 90 g. of the bromo compound yielded 22 g. of the cyclopropane melting at 137°, 9 g. of the cyclopropane melting at 187°, 3.4 g. of the reduction product, 2.7 g. of diketone and 1.1 g. of unchanged bromo compound.

1-Anisoyl-2,3-diphenyl-2-nitro Cyclopropane, 111.—The higher-melting isomer is sparingly soluble in ether, alcohol and acetone, readily soluble in chloroform and in ethyl bromide. It crystallizes in flattened needles and melts at 187°.

Anal. Calcd. for $C_{23}H_{19}O_4N$: C, 74.0; H, 5.1. Found: C, 73.5; H, 5.2.

Ozonization.—A rapid current of ozonized oxygen containing about 6% of ozone was passed for two hours through a solution of one gram of the substance in ethyl bromide. The solution assumed a pale yellow color but remained clear. It was poured into water, the mixture was boiled for a short time, then distilled with steam; the distillate contained only ethyl bromide. The residue in the flask—a solid contaminated with a little yellow oil—was filtered. After washing with ether, the solid proved to be 0.86 g. of unchanged substance. The ether contained a little oil which was doubtless due to some general oxidation because a similar oil was obtained whenever any of these anisyl derivatives was subjected to prolonged action of ozone.

Behavior toward Bases.—The cyclopropane derivative is not attacked by organic bases; it was recovered after it had been boiled for twenty minutes with pyridine, piperidine and methyl alcoholic piperidine. A solution in methyl alcoholic ammonia slowly assumed a pale yellow tint, but the solid that was recovered by evaporating both ammonia and solvent still melted at 185–187°. Methyl alcoholic sodium hydroxide and sodium methylate act readily in the cold but in order to ensure complete conversion it is safest to warm the substance with a solution of the methylate.

A suspension of 2 g. of the finely ground material in 15 cc. of 5% sodium methylate was warmed for a few minutes on a steam-bath until solution was complete, then allowed to cool. It deposited a sodium compound in fine, yellow needles. These were collected on a glass filter and thoroughly washed with anhydrous ether; yield, 2.05 g.

The sodium compound, suspended in 5 cc. of ether, was shaken with iced dilute hydrochloric acid until completely colorless. After washing with ether and drying the solid suspended in the ethereal layer, it melted at 140°; yield, 1.1 g. When entirely free from acid this solid can be recrystallized without serious loss by dissolving it rapidly in boiling methyl alcohol and cooling the solution at once. The melting point steadily falls if the crystallization is slow, and when the solutions contain a trace of acid they deposit an isomeric product.

Anal. Calcd for $C_{23}H_{19}O_4N$: C, 74.0; H, 5.1. Found: C, 73.8; H, 5.2.

α-Benzal-α-anisoyl-β-phenyl-β-nitro Ethane, **VII.**—The rearrangement product crystallizes in small, thin needles. It is sparingly soluble in ether and in cold methyl alcohol, readily soluble in boiling alcohols. Its solution in cold concentrated sodium methylate deposits the yellow sodium compound in needles. Solutions in alcoholic sodium hydroxide gradually turn red and then smell of benzaldehyde.

Ozonization.—Ozonized oxygen containing about 6% of ozone was passed for half an hour through a solution of one gram of the substance in ethyl bromide. The ozonized solution was poured into water, the mixture warmed to remove the ethyl bromide, boiled for a few minutes, then distilled with steam. Drops of liquid which had the odor of benzaldehyde collected in the distillate. The presence of benzaldehyde was confirmed by adding semicarbazide and comparing the resulting semicarbazone with an authentic specimen.

The Isomeric Ethylene Derivative.—The ethereal solution from which the product melting at 140° had been removed gradually deposited another colorless product which had a lower melting point. After several recrystallizations from methyl alcohol this was obtained in the form of lustrous prisms which melted at 118°. The same substance was obtained also by repeated recrystallization of the higher-melting compound and by one crystallization from methyl alcohol containing a trace of acetic acid.

Anal. Calcd. for $C_{23}H_{19}O_4N$: C, 74.0; H, 5.1. Found: C, 74.2; H, 5.1.

The isomer is readily soluble in ether and methyl alcohol. Its solution in cold concentrated sodium methylate deposits a yellow sodium compound which crystallizes in stout prisms and which on acidification regenerates the lower-melting compound. This substance, when ozonized in the same manner as the preceding one, likewise gave benzaldehyde as one of the products. Since neither of these substances gives the reactions of isonitro compounds, they must be the geometrical isomers represented by formula VII.

The Lower-Melting Cyclopropane Derivative, 111.—The lower-melting isomer is readily soluble in chloroform and in acetone, moderately soluble in boiling methyl alcohol, sparingly soluble in cold alcohol and ether. It crystallizes in thick needles or prisms and melts at **137".** Its behavior when ozonized in ethyl bromide was exactly the same as that of the higher melting isomer.

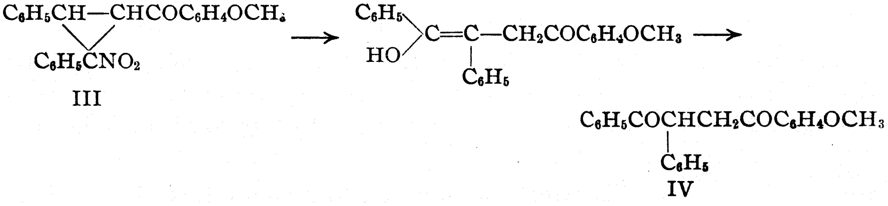
Anal. Calcd. for $C_{23}H_{19}O_4N$: C, **74.0;** H, **5.1.** Found: C, **73.8;** H, **5.2.**

Action of Bases.—The substance is altered by alcoholic ammonia, primary and secondary amines, alcoholic sodium hydroxide and alcoholates. All of these remove nitrous acid and open the cyclopropane ring but the nature of the organic product varies with the reagent and the solvent. In the presence of methyl alcohol one of the products is always a methoxyl compound. This can be obtained quantitatively by using a solution of sodium methylate in perfectly dry methyl alcohol.

A slightly warm 5% solution of sodium methylate was added, in **3** times the calculated quantity, to **3** g. of the finely powdered substance. This dissolved immediately and the very pale yellow solution soon deposited a crystalline solid. It was set aside for several hours, then filtered. The yield of washed and dried solid was 2.4 g. The diluted filtrate deposited 0.2 **g.** more of somewhat less pure material. The solid was recrystallized from methyl alcohol, from which it separated in long, thin needles melting at 144–145°.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.4; H, 6.0. Found: C, 80.1; H, **6.2.**

β,γ-Diphenyl-γ-Methoxy Allyl Anisyl Ketone, **VIII.—The** unsaturated ketone is readily soluble in methyl alcohol, less soluble in ether. It is not altered by dilute solutions of bases but it is extremely sensitive to acids. None of it can be recovered from a solution in methyl alcohol containing a drop of acetic acid; the solution deposits only the diketone IV, and when dry hydrogen chloride is substituted for the acetic acid, the principal product is the furane V. The diketone IV also generally appears as one of the products of the reaction even when contact with acid is carefully avoided, but its origin then is different. Its formation is due to the presence of sodium hydroxide in the alcoholate, and hence it becomes the principal product when methyl alcoholic sodium hydroxide is substituted for the methylate.


III

IV

Ozonization.—A current of ozonized oxygen containing about 6% of ozone was passed for an hour through a solution of **2** g. of the methoxyl compound in ethyl bromide. The solution was poured into water, the mixture freed from ethyl bromide and distilled with steam. The distillate, which contained drops of an oil that had the odor of methyl benzoate, was extracted with ether, the extract freed from acid by extraction with sodium carbonate, then evaporated. Half of the residue when hydrolyzed gave pure benzoic acid; the remainder gave benzamide when warmed with alcoholic ammonia.

The residue left after the methyl benzoate had been distilled with steam was extracted with ether. The ethereal solution was freed from acid by extraction with bicarbonate, then shaken with saturated aqueous copper acetate. It deposited a greenish-yellow copper compound which on acidification turned into a pale yellow solid crystallizing in plates melting at 129°. As the yield of this product was only 0.11 g. it seemed wise to synthesize benzoyl anisoyl methane for comparison. This was readily accomplished by adding bromine to benzal acetyl anisole, boiling the dibromide with sodium alcoholate and digesting the resulting ethoxyl compound with acetic acid

$$C_6H_5CHBrCHBrCOC_6H_4OCH_3 \longrightarrow C_6H_5C(OC_2H_5){=}CHCOC_6H_4OCH_3 \longrightarrow C_6H_5COCH_2COC_6H_4OCH_3$$

Both the diketone obtained in this manner and a mixture of the synthetic and the ozonization product melted at 129°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.5. Found: C, 75.5; H, 5.6.

The ethoxyl compound corresponding to the methoxyl compound VIII.—For the sake of comparison, the low-melting cyclopropane derivative was treated also with sodium ethylate. It dissolved just as readily but the product separated much more slowly. It was recrystallized from absolute ethyl alcohol from which it separated in colorless cubical prisms melting at 89–90°.

Anal. Calcd. for $C_{25}H_{24}O_3$: *C*, 80.6; H, 6.4. Found: C, 80.6; H, 6.5.

Summary

The paper contains:

1. A method for the preparation of cyclopropane derivatives in which a tertiary nitro group is attached to one of the carbon atoms of the ring.
2. An account of the behavior of cyclopropane derivatives of this type toward bases.

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[CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORY OF THE DEPARTMENT OF PHYSICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

THE RELATIONS BETWEEN SOME PHYSICAL PROPERTIES AND THE CONSTITUTION OF CERTAIN NAPHTHALENE DERIVATIVES

BY HENRY DE LASZLO

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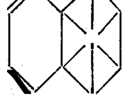
The structural formula of naphthalene is a vexing problem that has called forth a number of suggestions, more especially in recent years. Harries,[1] Mayer and Bansa,[2] and others suggest an aromatic olefinic structure . Willstätter[3] was inclined to support this view, but admitted later[4] that it is not necessarily right. On the other hand, v. Wein-

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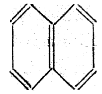
[1] Harries, Ann., 343,337 (1905).

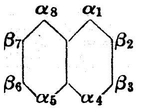
[2] Mayer and Bansa, *Ber.*, 54, 19 (1921).

[3] Willstätter, *Ber.*, 44, 3430 (1911).

[4] Willstätter, *Ber.*, 56, 1407 (1923).

berg[5] is strongly in favor of the absolutely symmetrical, non-rigid Erlenmeyer-Graebe formula  based on his experience in the formation of azo colors. This view is supported by Lesser[6] on purely chemical grounds in the case of the same molecule. Lastly, v. Auwers[7,8] produces evidence for a formula in which the α and β positions are optically and chemically equivalent, both halves of the molecule being of the same type. It will be shown later that our results agree substantially with those obtained by v. Auwers.

The examination of the absorption spectra of a number of mono-substitution products of naphthalene[9] showed that the alpha derivatives were optically clearly differentiated from the beta compounds, the spectra of the latter being more like that of the parent body[10] than the former. This fact, among others, led us to measure the absorption spectra of the ten isomeric dichloronaphthalenes, both in vapor and solution. Throughout this paper we designate the position of the chlorine atoms in the naphthalene skeleton as shown, since we find that this expresses the optical characteristics of the isomers better than numbering alone. We hoped thus to obtain evidence as to whether the two halves of the naphthalene molecule were symmetrically built or not.



Technique.—The ten dichloronaphthalenes were kindly lent to me by Professor Palmer Wynne of Sheffield University, England. These substances had been prepared synthetically in the course of Armstrong and Wynne's[11] researches, so that there can be no doubt as to their chemical structure. They were all recrystallized at least three times from optically pure hexane,[12] and were thus obtained in perfectly white crystals which, however, could be easily differentiated. We hope later to prepare some more material, and then endeavor to grow crystals large enough for both x-ray and crystallographic investigation. These purified specimens have proved to be very stable when exposed to both light and air.

All the solution spectra were taken with hexane[12] as the solvent, using V. Henri's technique[13] for obtaining the molecular extinction coefficients (2). We sought to increase the accuracy of this method, which depends on the constancy of the source of

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[5] A. v. Weinberg, *Ber.*, 54,2168 (1921).

[6] Lesser, *Ber.*, 58,2109 (1925).

[7] K. v. Auwers and Frühling, *Ann.*, 422,206 (1921).

[8] K. v. Anwers and Krollpfeiffer, *Ann.*, 430,243 (1923).

[9] H. de Laszlo, *Proc. Roy. Soc. (London)*, 111, 355 (1926).

[10] H. de Laszlo, *Z. physik. Chem.*, 118,371 (1925).

[11] Armstrong and Wynne, *Chem. News*, 59, 189 (1889); 60, 58 (1889); 61, 273 (1890); 93, 76, 70 (1906).

[12] V. Henri and Castille, *Bull. soc. chim. biol.*, 6, 299 (1924).

[13] V. Henri, "Études de photochemie," Gauthier-Villars, Paris, 1919.

light, by inserting a rotating spark gap[14] in series with the one used in the experiment. To obtain a good continuous source of ultraviolet light, we supplemented the underwater spark, in which duralumin electrodes were used, by a gas-filled tungsten lamp which was made up for us through the kindness of Mr. A. L. Kimball, Jr., of the General Electric Company, Schenectady. The lamp consisted of a piece of tungsten ribbon (T) about 2 cm. long, 1.5 mm. wide, and 0.1 mm. thick, welded to two stout tungsten or nickel supports (S). The light issued through a fused quartz window (W) (3 cm. diam.) which was attached by means of a graded seal (G) to the body of the lamp at about 6 inches from the filament, to avoid deposition of tungsten by evaporation. It took about 18-20 amperes at 6 volts to run it. In order to bring it up to its maximum brightness, the filament was compared with that of a standard gas-filled lamp on a photometer bench and the current increased until they were equally bright. The experimental lamp was then run with a 10-15% current overload at about 300° below the melting point of tungsten. We were thus enabled to get a perfectly continuous blackening of the photographic plate down to 2500 Å., it proving especially satisfactory around 3000 Å.

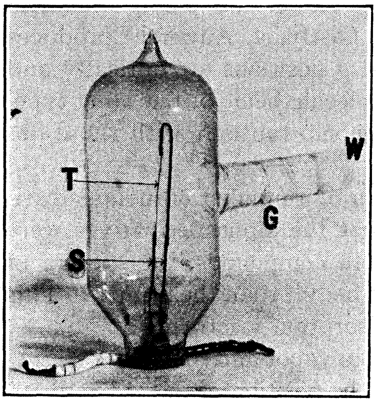

Fig. 1.

The vapor spectra were examined in an improved form of apparatus (see Fig. 2) over that described previously.[10] It was entirely constructed of fused quartz. The

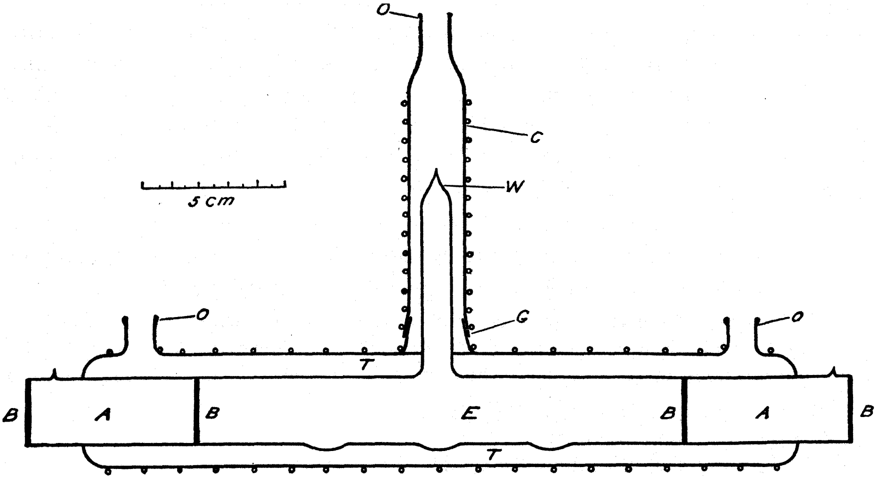

Fig. 2.

spaces (A) are evacuated, thus preventing condensation of the substance on the transparent windows (B). The outside is heated with Chromel wire, the mercury in the interannular space T being there to distribute the heat, thus bringing the vapor tube E to a constant temperature for any specified current. The material is inserted through a

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[14] H. de Laszlo, THIS JOURNAL, 49, 2107 (1927); *Ind. Eng. Chem.*, 19, 1366 (1927).

side tube (W) which is sealed off after evacuating. A tube C is then fitted over a ground joint (G), the space between G and W being filled with mercury. C is heated about 50° higher than the rest of the apparatus by winding the Chromel closer. This insures that the substance does not distil into the side tube. Photographs are taken at every 10°, the temperature being measured with a thermocouple inserted through O. The openings O,O,O are connected to a three-way tube which leads to an exhaust line. so that mercury vapor does not enter the laboratory. The optical equipment consisted of a Hilger E_2 quartz spectrograph, the wooden back of which had been changed to metal owing to warping through atmospheric influence.

The results of our researches are shown graphically on Figs. 3, 4 and 5. Tables I, II and III give the exact position (λ) and intensity (Σ) of the bands both in vapor and solution.

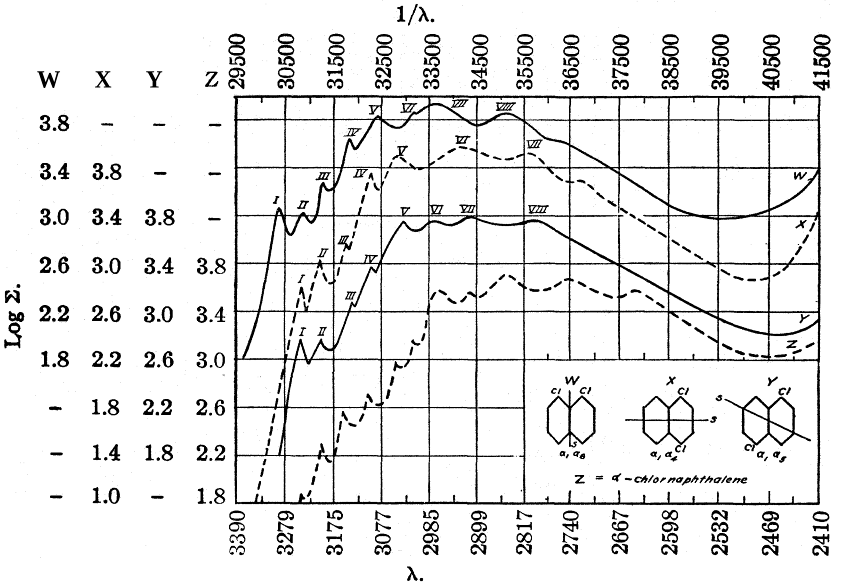


Fig. 3.

General Characteristics.—The curves and tables show: (A) that all the absorption spectra can be divided into two distinct parts, each possessing entirely different properties. (B) Two common frequency intervals Δ_1 and Δ_2 occur in all the isomers. (C) The spectra are of three definite types, each of which is represented in Figs. 3, 4 and 5.

(A). Part I between λ 3295 Å. and λ 2980 Å. consists of a number of narrow, clearly defined bands whose maxima may be determined with an accuracy of ±1 Å. These, according to present-day theory, are due to the quantized vibration of certain atoms or groups of atoms in the molecule.

Part II between λ 3080 Å. and λ 2530 Å. is of a very different character. The bands are between 50 Å. and 100 Å. wide, their maxima being difficult to measure with an accuracy greater than ±3 Å. We are as yet not certain what gives rise to this type of band, but it is suggested that the molecule becomes activated by quanta received from the light source used in these determinations and that those electron orbits which hold the atoms of the molecule together are altered, thus causing a general rearrangement of the structure in order to bring the molecule into equilibrium again. But this new state is not as stable as the first and becomes labile, for the molecule will be constantly changing its form between certain limits; vibrational quantization ceases and the bands become broad.

These spectra possess two more properties which make it easy to separate them into two parts.

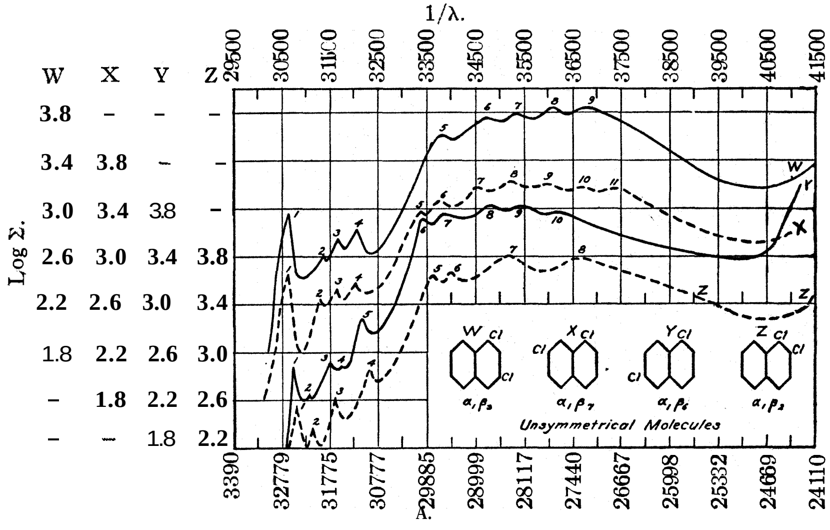


Fig. 4.

(a) We have found, as in the case of the mono-derivatives of naphthalene, that the vapor bands reproduce the hexanic solution bands both in relative position and intensity, except that the latter are shifted towards the red with respect to the former. This shift (6) is a constant for each part of the spectrum of every isomer, and the various values are shown in Table IV. This rule has been found to hold rigorously in the case of substances whose vapor spectra do not show any fine structure. *But 6 is widely different for both parts, it being **always** larger for Part II than Part I.* We have sometimes used this observation as a check on the exact position of some band that is but faintly distinguishable in solution or *vice versa.* How useful this may be is seen in the case of $\alpha_1\beta_7$ and $\alpha_1\beta_3$. Here both solution spectra were practically identical, especially in Part I. This, coupled with the fact that their melting points differed by but 1°, led to the supposition that they were perhaps not pure. However, on photographing the vapor spectra, δ for Part II of $\alpha_1\beta_7$ was found to be about double that for $\alpha_1\beta_3$, thus clearly showing that no such error had arisen.

(b) The molecular absorption coefficient (2) of Part II is about ten times stronger than Part I, which again supports the theory that the molecule becomes unstable on activation, for it has been found that those bodies which are chemically the most unsaturated or unstable have the strongest ultraviolet absorption bands.

No case of fine structure of the vapor bands could be found. This is interesting, as traces of such were noted for some of the bands of the monochloronaphthalenes. Thus rotational quantization ceases with the introduction of the second chlorine atom.

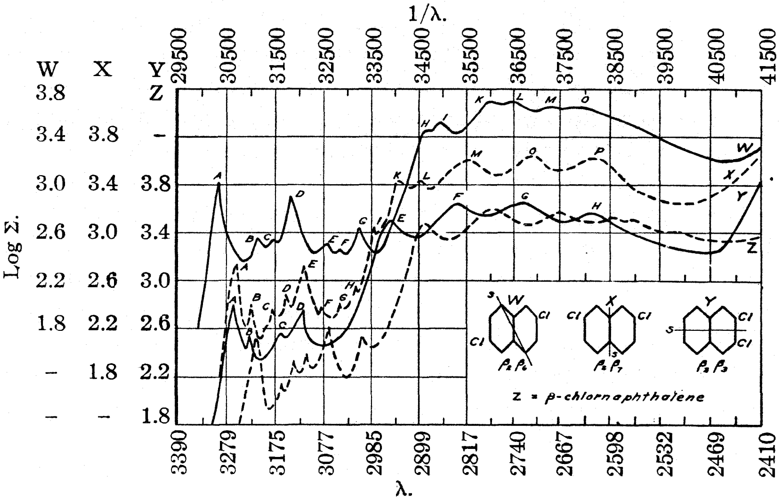
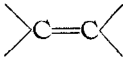


Fig. 5.

The first band that was found in Part I of each of the ten isomers corresponds to the characteristic band (c) of naphthalene (**32605** cm.$^{-1}$, Σ = **320**). It shifts in the spectrum between the limits λ **3292** Å. and λ **3245** Å., and is most clearly marked in the case of the β,β and α,β derivatives.

Going out from this band we find a common frequency interval Δ_1 varying from **1400** to **1450** cm.$^{-1}$. The only exception to this is the $\alpha_1\beta_2$ compound which shows one of **1530** cm.$^{-1}$. The same interval in naphthalene was found to be **1458** cm.$^{-1}$, so that the introduction of two chlorine atoms in one or both halves of the molecule would seem to make but little difference. The origin must lie in certain quantized electron jumps belonging to such an atom or groups of atoms as are unlikely to be affected to any great extent by the introduction of two substituents of fairly high atomic weight and negative moment. This might, therefore, originate in the  linkage which acts as a pivot for both halves of the molecule.

A smaller interval Δ_2 of amazing regularity was found among most of the members of this group. This varied from 395 – 530 cm.$^{-1}$. Naphthalene has one of 474 cm.$^{-1}$ which lies nearly midway between the above limits. Here, however, there is a distinct difference depending on whether the chlorine atoms are in one or both rings. The results for Δ_1 and Δ_2 are summarized in Table IV. It is useless at present to theorize on the origin of these intervals; but we feel that much light would be thrown on the question by measuring the absorption spectra of (a) the twenty di-substituted naphthalenes, where both substituents were either fluorine or bromine atoms and (b) where fluorine and bromine are both present in the molecule in all the possible fourteen combinations. One might thus get some clue as to the mechanism of their formation by observing what changes were then wrought in the frequency intervals by such atoms of the same type but widely different atomic weights and electric moments under these several conditions.

(c) On examining the curves of the solution spectra we find that they may be divided into three clearly differentiated groups, the members of each group being of the same general type, namely, α,α, α,β and β,β. Besides this we will see how the average Σ rises in steps from β,β to α,α and conversely how the breadth of Part I decreases. The former property may be brought into line with the fact that Σ rises with the instability of the compound. α,α derivatives are more readily oxidized than β,β.

	Average Σ		
	Part I	Part II	Breadth, Part I
(a) α,α	1500	7000	1500 cm $^{-1}$
(b) α,β	500	5000	2200 cm $^{-1}$
(c) β,β.	400	3500	3000 cm $^{-1}$

We will now attempt to analyze successively each member of the three groups.

TABLE I

ABSORPTION BANDS OF THE α,α-DICHLORONAPHTHALENES

$\alpha_1\alpha_8$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	I	3285	1150	30440	115°	3226	30630
	II	3238	1050	30880		3219	31070
	III	3193	1850	31320		3174	31510
	IV	3140	4400	31850		3121	32040
Pt. II		3078	6950	32410	90°	3027	33040
	I	3021	7250	33110		2972	33650
	VII	2964	8350	33700		2908	34390
	VIII	2849	7150	35100		2899	34490

TABLE I (Concluded)

$\alpha_1\alpha_4$

		Solution				Vapor	
		λ	Σ	1/λ		λ	1/λ
Pt. I	(?.	3245	620	30820	105°	3229	30970
	II	3205	1080	31200		3190	31350
	III	3151	1450	31740		3136	31890
	IV	3099	5500	32270		3085	32410
II	V	3048	7950	32810	70°	2980	33560
	VI	2926	9100	34180		2863	34930
	VII	2810	8350	35590		2752	36340
	VIII	2712	4900	30870		2651	37720

$\alpha_1\alpha_5$

		Solution				Vapor	
		λ	Σ	1/λ		λ	1/λ
Pt. I	I	3244	620	30830	140°	3226	31000
	II	3199	605	31260		3181	31440
	III	3139	1200	31860		3121	32040
	IV	3097	2350	32290		3082	32450
Pt. II	V	3033	5600	32970	80°	2978	33580
	VI	2979	5750	33570		2926	34180
	VII	2915	6200	34310		2863	34930
	VIII	2799	5800	35730		2750	36380

(a) The α,α group shown on Fig. 3 is the least like the spectrum of naphthalene. On the other hand, it bears a marked resemblance to a-chloronaphthalene, whose absorption curve is given on the same figure for purposes of comparison. None of the bands are very well marked and the two parts of the spectrum form in general a smooth curve without any clear division.

It is of special interest to notice how similar are the first parts of $\alpha_1\alpha_4$ and $\alpha_1\alpha_5$. Here, in the first case, the two chlorine atoms are substituted in the same ring, and in the second case in both rings. This fact would seem to show that the two halves of the naphthalene molecule are symmetrically built, or at least that the a positions are optically as well as chemically equivalent to each other.

The (Δ_1) is about 1440 cm.$^{-1}$, (Δ_2) about 435 cm.$^{-1}$ when the chlorine atoms are in opposite halves, and 535 cm.$^{-1}$ when substituted in the same half.

	No.	Δ_1	No.	Δ_2	No	Δ_2
$\alpha_1\alpha_8$	I–IV	= 1410 cm.$^{-1}$	I –II	= 440 cm.$^{-1}$	II–III	= 440 cm.$^{-1}$
$\alpha_1\alpha_4$	I–IV	= 1450 cm.$^{-1}$	II–III	= 540 cm.$^{-1}$	III–IV	= 530 cm.$^{-1}$
$\alpha_1\alpha_5$	I–IV	= 1460 cm.$^{-1}$	I –II	= 430 cm.$^{-1}$	III–IV	= 430 cm.$^{-1}$

TABLE II

ABSORPTION BANDS OF α,β-DICHLORONAPHTHALENES

$\alpha_1\beta_3$

		Solution				Vapor	
	No	λ	Σ	1/λ		A	1/λ
Pt I	1	3264	915	30650	150°	3248	30790
	2	3187	400	31380		3173	31520
	3	3158	355	31670		3145	31800
	4	3120	675	32050		3107	32190

TABLE II *(Concluded)*

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. II	5	2949	4000	33910	85°	2901	34470
	6	2876	5500	34770		2834	35290
	7	2833	6050	35300		2788	35870
	8	2770	6700	36100		2730	36630
	9	2720	6600	36760		2680	37310
				$\alpha_1\beta_7$			
Pt. I	1	3264	730	30650	160°	3247	30800
	2	3195	455	31300		3180	31450
	3	3157	555	31680		3140	31830
	4	3120	620	32050		3106	32200
	5	2991	2400	33430		2975	33610
Pt. II	6	2960	2800	33780	95"	2860	34960
	7	2895	3800	34540		2799	35730
	8	2840	4300	35210		2748	36390
	9	2778	4000	36000		2690	37170
	10	2727	3800	36670		2641	37860
	11	2673	3700	37420		2590	38610
				$\alpha_1\beta_6$			
Pt. I	1	3253	300	30740	150"	3234	30920
	2	3219	185	31070		3201	31240
	3	3174	330	31510		3156	31690
	4	3151	305	31740		..	...
	5	3107	760	32190		3091	32360
Pt. II	6	2992	5050	33420	75"	2913	34340
	7	2957	5750	33820		2880	34720
	8	2876	6750	34770		2804	35660
	9	2885	6600	35370		2767	36140
	10	2764	5800	36180		..	...
				$\alpha_1\beta_2$			
Pt. I	1	3245	305	30820	135"	3226	31000
	2	3212	240	31130		3194	31310
	3	3162	435	31630		3145	31800
	4	3091	725	32350		3073	32530
Pt. II	5	2976	4500	33600	75°	2892	34580
	6	2943	4700	33980		2860	34960
	7	2842	6300	35150		2766	36150
	8	2731	6200	36610		2666	36510

(b) The four α,β compounds shown in Fig. 4 possess a marked similarity. Thus $\alpha_1\beta_3$ and $\alpha_1\beta_7$ are nearly identical, although in the former both chlorines are in the same ring and in the latter in both rings. Similarly, $\alpha_1\beta_2$ and $\alpha_1\beta_6$ are not very unlike, yet here again the substituent atoms are distributed first on one side, then on both sides of the molecule. This should surely prove the symmetrical structure of the two halves of the molecule and the optical equivalence of the β_3 and β_7 as well as of the β_2 and β_6 positions.

Δ_1 recurs with its usual value except for $\alpha_1\beta_2$, which is far higher than for any of the others. Δ_2 is not so regular as in the α,α and β,β types. There is a considerable difference between the $\alpha_1\beta_7$ and $\alpha_1\beta_6$, as is borne out by the spectra. The values of Δ_2 for $\alpha_1\beta_3$ and $\alpha_1\beta_2$ may not be correct, but their similarity is striking and seems to agree with what was found above for the α,α group, in that Δ_2 *increases when the atoms are distributed between the two rings.*

	No.	Δ_1	No.	Δ_2
$\alpha_1\beta_3$	1 4	= 1400 cm.$^{-1}$	1–2	= 730 cm.$^{-1}$
$\alpha_1\beta_7$	1–4	= 1400 cm.$^{-1}$	2–3	= 380 cm.$^{-1}$
	4–5	= 1400 cm.$^{-1}$	3–4	= 370 cm $^{-1}$
$\alpha_1\beta_6$	1–5	= 1445 cm.$^{-1}$	2–3	= 440 cm.$^{-1}$
			4–5	= 450 cm.$^{-1}$
α_{1i32}	1 4	= 1530 cm.$^{-1}$	3 4	= 720 cm.$^{-1}$

TABLE III

ABSORPTION BANDS OF THE β,β-DICHLORONAPHTHALENES

$\beta_2\beta_6$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
Pt. I	A	3292	1000	30380	155°	3272	30570
	B	3213	365	31120		3193	31320
	C	3183	345	31420		3164	31610
	D	3144	795	31810		3125	32000
	E	3072	325	32550		3053	32750
	F	3046	290	32830		3029	33010
	G	3008	440	33240		2992	33420
Pt. II		2893	2900	34570	110°	(2829	35350
		2867	3350	34880		2804	35660
		2780	5000	35970		2720	36760
		2751	5000	36350		2692	37150
	M	2682	4600	37290		2623	38120
		2649	4450	37750		..	...

$\beta_2\beta_7$

		Solution				Vapor	
	No.	λ	Σ	1/λ		λ	1/λ
I't. I	A	3256	550	30710	145°	3239	30870
	B	3223	250	31030		3207	31180
	C	3182	230	31430		3167	31580
	D	3151	310	31740		3134	31910
	E	3111	550	32140		3096	32300
	F	3080	240	32470		3065	32630
	G	3045	250	32840		3031	32990
	H	3015	365	33170		3000	33330
	I	2979	1150	33570		2965	33730
Pt. II	K	2934	2600	34080	85°	2866	34890
	I,	2897	2600	34520		2831	35320
	M	2819	4000	35470		2756	36290
	O	2707	4350	36940		2650	37740
	P	2615	4200	38240		2560	39060

TABLE III (Concluded)

$\beta_2\beta_3$

	No.	Solution λ	Σ	1/λ		Vapor λ	1/λ
Pt. I	A	3260	635	30680	140°	3244	30840
	B	3226	350	31000		3209	31160
	C	3163	365	31630		3148	31770
	D	3115	575	32100		3100	32260
II	E	2947	3150	33930		2878	34750
	F	2830	4350	35340		2766	36150
	G	2721	4350	36750		2662	37570
	H	2618	3650	38200		2563	39020

(c) The β,β group stands out by the clearness and persistence of the bands of Part I, which reminds one forcibly of parabenzene derivatives. Thus both *p*-dichlorobenzene[15] and *p*-xylene[16] have three very persistent and clear bands far stronger than the respective ortho and meta compounds. The resemblance to the curve of β-chloronaphthalene is very striking. In the case of 82/36 and $\beta_2\beta_7$ it seems to have broadened considerably add we obtain a double period for Δ_1. This is the same phenomenon that was found for β_2,β_6-dimethylnaphthalene.[17] Δ_1 is well represented and Δ_2 is likewise clearly marked.

	No.	Δ_1	No.	Δ_2
	A–D	= 1430 cm.$^{-1}$		
	B–E	= 1430 cm.$^{-1}$	C–D	= 390 cm.$^{-1}$
	C–F	= 1410 cm.$^{-1}$	F–G	= 390 cm.$^{-1}$
	D–G	= 1430 cm.$^{-1}$		
$\beta_2\beta_7$	A–D	= 1430 cm.$^{-1}$	B–C	= 400 cm.$^{-1}$
	D–I	= 1430 cm.$^{-1}$	D–E	= 400 cm.$^{-1}$
	B–F	= 1440 cm.$^{-1}$	H–I	= 400 cm.$^{-1}$
	C–G	= 1410 cm.$^{-1}$		
$\beta_2\beta_3$	A–D	= 1420 cm.$^{-1}$	C–D	= 470 cm.$^{-1}$

Δ_2 is nearly the same in the two isomers where the chlorines are on opposite halves of the molecule; but this value is smaller in $\beta_2\beta_3$ where the substitucnt atoms are adjacent.

Other Physical Properties of the Dichloronaphthalenes Refractive Indices.—We have just shown how one can divide these isomers into three types with the aid of their absorption spectra. The measurement of the specific exaltation of refractivity ($E\Sigma_D^{20°}$) by v. Auwers and Krollpfeiffer[18] for a number of these compounds has given similar results. Unfortunately they did not measure the whole series so as to confirm their conclusions. As will be seen from Table IV, the $E\Sigma_D^{20°}$ values are arranged in the following order, $\beta,\beta > \alpha,\beta > \alpha,\alpha$. Thus the effect previously noted by v. Auwers

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[15] Jan. Kalff, "Die Refractometrie der Chlorbenzolen," *Dissertation*, Amsterdam, 1924.

[16] Klingstedt, *Compt. rend.*, 175, 1065 (1922).

[17] De Laszlo, *ibid.*, 180, 203 (1925).

[18] K. v. Auwers and Krollpfeiffer, Ann., 422, 168 (1921).

TABLE IV

SOME PHYSICAL CONSTANTS OF THE DICHLORONAPHTHALENES

	6 in cm.$^{-1}$		Δ_1 in cm.$^{-1}$	Δ_2 in cm.$^{-1}$	$E\Sigma^{20°}_D$	M. p., °C		
	Part *I*	Part *II*				$(Cl)_2$	$(Br)_2$	
$\beta_2\beta_6$	190	790	1426	390	...	135	158	[a]
$\beta_2\beta_7$	160	820	1430	400	...	120	...	
$\beta_2\beta_3$	160	810	1420	470	1.3	114	140	
$\alpha_1\alpha_5$	170	620	1455	430	0.9	107	131	
$\alpha_1\alpha_8$	190	000	1410	440	1.1	87	109	
$\alpha_1\alpha_4$	150	750	1445	630	0.9	68	82	
$\alpha_1\beta_7$	150	1180	1400	375	1.1	63	75	[b]
$\alpha_1\beta_8$	140	560	1400	730	...	62	64	
$\alpha_1\beta_6$	180	900	1445	445	...	49	61	
$\alpha_1\beta_2$	180	990	1530	720	1.0	35	67	
Naphthalene	260	505	1458	474	1 9	80 3		

[a] Symmetrical molecules.

[b] Unsymmetrical molecules.

that, in the case of the mono derivatives of naphthalene, the $E\Sigma$ value was always greater for the beta compounds is confirmed in the di-series. Judging from the previous values[18] found for the dichlorobenzenes, and xylenes, in which the para compounds had the highest $E\Sigma^{20°}_D$, we would likewise expect the $\beta_2\beta_6$ dichloronaphthalene to show a similar maximum in this respect, since its structure is comparable to a para-benzene derivative. As was the case with the absorption spectra, the values of $\alpha_1\alpha_4$ and $\alpha_1\alpha_5$ are identical where the chlorine atoms are in one, and later, in two rings. Hence v. Auwers deduces that naphthalene is a symmetrical system in which the four α and four β positions, respectively, are optically as well as chemically equivalent. At the same time it shows that there is a great difference between the alpha and beta position both from an optical and chemical point of view. It should also be noted that the $E\Sigma^{20°}_D$ value, and hence the structure of the $\beta_2\beta_3$ compound, is nearer to that for naphthalene than are the α,α bodies. This is borne out by our measurement of the absorption curves.

Melting Point.—Korner was the first to observe that in the case of the di-substitution product of benzene, the para derivatives always had the highest melting point. In 1882 Carnelley[19] made the suggestion that those isomers whose structures were the most compact and symmetrical would have the highest melting points. This rule was based on his knowledge of members of the benzene and aliphatic series but did not include naphthalene derivatives. We have previously noted,[9] that in the case of the mono-substitution products of naphthalene, the β compound melts higher than the α. We find that the ten isomeric dichloro- and dibromonaphthalenes (see Table IV) may be ordered into three groups, namely, $\beta,\beta > \alpha,\alpha > \alpha,\beta$ where the $\beta_2\beta_6$ compounds always have the highest melting point. The latter part of the rule seems also to hold

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[19] Carnelley, *Phil.* Mag., **13,** 116 **(1882).**

for $(OH)_2$, $(NH_2)_2$, $(CH_3)_2$, $(CN)_2$ and $(NO_2)_2$ dinaphthalene derivatives, in so far as their isomeric forms have been investigated. We would add that, assuming the conventional plane formula for naphthalene, then the $\beta_2\beta_6$ position possesses a marked degree of symmetry, and at the same time the substituent atoms are as far apart as possible, in a position in fact that is analogous to the para compounds of the benzene series.

On reviewing all the melting points and Figs. 5 and **3,** we see that it is possible to place a plane of symmetry (S) through the plane formulas of all the β,β and a,a isomers, which at the same time all show higher melting points than the α,β compounds. The latter exhibit no degree of symmetry.

Thus Carnelley's rule may be applied to members of the naphthalene series.

Summary

A. The investigation of the absorption spectra of the dichloronaphthalenes has shown that any structural formulas which may be evolved for them must conform to three conditions:

(1) Both halves of the molecule are symmetrical in structure.

(2) The four alpha positions are optically equal.

(3) The two pairs of beta positions, $\beta_3\beta_7$ and $\beta_2\beta_6$, are not quite equivalent, the members of each pair, however, being equal to each other.

B. All the isomers show two frequency intervals. The larger approximates closely to that found for naphthalene, and the smaller varies considerably depending on the position of substituent atoms.

C. The melting point of the $\beta_2\beta_6$ compound for a great variety of di-substituted naphthalenes is the highest in any particular set of isomers. The unsymmetrical α,β derivatives have a lower melting point than the symmetrical β,β and α,α compounds.

CAMBRIDGE, MASSACHUSETTS

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

THE BEHAVIOR OF 2-PHENYL SEMICARBAZONES UPON OXIDATION

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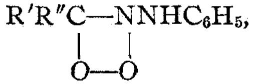
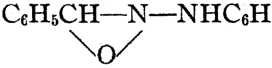
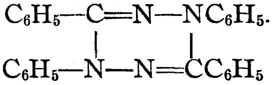
The class of compounds known as hydrazones, and in particular phenylhydrazones such as benzal phenylhydrazone, yield several different types of oxidation products. Certain aldehyde and ketone phenyl- and hexahydrophenylhydrazones yield, through the action of even atmospheric oxygen, peroxides of the general formula,[1]  $R'R''C-NNHC_6H_5$ (with $O-O$), while quite recently it has been observed that benzal phenylhydrazone, oxidized with benzoyl superoxide, is converted to benzal phenylhydrazone oxide,  $C_6H_5CH-N-NHC_6H_5$.[2] Benzophenone phenylhydrazone shows a similar behavior, but the reaction apparently cannot be extended to aliphatic phenylhydrazones.

In addition to the above reactions of benzal phenylhydrazone, the oxidation, depending on the conditions of the experiment, may proceed with the elimination of hydrogen between two molecules, and here four distinct products have been isolated: (I) dibenzal diphenyl dihydrotetrazone, $C_6H_5CH{=}NN(C_6H_5)NC_6H_5N{=}CHC_6H_5$;[3] (II) benzil phenyl osazone, $C_6H_5NHN{=}C(C_6H_5)C(C_6H_5){=}NNHC_6H_5$;[4] (III) dehydrobenzal phenylhydrazone, $C_6H_5NHN{=}C(C_6H_5)N(C_6H_5)N{=}CHC_6H_5$;[5] and (IV) 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine,[6]  $C_6H_5-C{=}N-NC_6H_5$ / $C_6H_5-N-N{=}CC_6H_5$.

As von Pechmann points out, a combination of the reactions involved in the preparation of Products I and II might be expected to result in the formation of a 1,2,3,4-tetrazine, that is, a so-called osotetrazone. However, it has developed that only aliphatic aldehyde phenylhydrazones yield final oxidation products of this type;[7] for instance, acetaldehyde phenylhydrazone goes to diacetyl phenyl osazone, and this on further oxidation with potassium dichromate in acetic acid solution is converted to 5,6-

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[1] Busch and Dietz, *Ber.*, **47,3277 (1914)**; Harkins and Lochte, THIS JOURNAL **46, 450 (1924)**; Busch and Linsenmeier, *J. prakt. Chem.*, **115,216 (1927)**.

[2] Bergmann, Ulpts and Witte, *Ber.*, **56,679 (1923)**.

[3] Von Pechmann, *Ber.*, **26,1045 (1893)**.

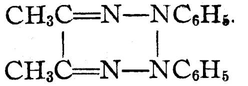
[4] Ingle and Mann, *J. Chem. Soc.*, **67,606 (1895)**.

[5] Minnuni and Rapp, *Gazz. chim. ital.*, **26,** I, 441 **(1896)**.

[6] Bamberger and Grob, *Ber.*, **34,526 (1901)**.

[7] Von Pechmann, *Ber.*, **21,2751 (1888)**.

dimethyl-2,3-diphenyl-2,3-dihydro-1,2,3,4-tetrazine,



From the above discussion it is evident that in the oxidation of phenylhydrazones seven distinct types of compounds have been prepared, six of which are represented among the oxidation products of benzal phenylhydrazone. Two of the reactions involved here are simple additive reactions, while in the five others two molecules of the hydrazone are united by the removal of either two or four hydrogens from two molecules of the hydrazone as shown above.

It has been recently observed that acetone 2-phenyl semicarbazone, $C_6H_5N(CONH_2)N{=}C(CH_3)_2$, "reacts readily with potassium permanganate in acetone with the formation of a beautifully crystallizing yellow compound."[8] This rather unexpected reaction, which was not further studied at the time, gave rise to the present investigation.

The analytical data and a molecular weight determination show that the substance discovered by Goodwin and Bailey, and which will be referred to hereafter in this paper as "Product A," corresponds to the formula, $C_{17}H_{21}ON_5$. Its chemical behavior, taken in connection with the formula, leads to the conclusion that in the oxidation of acetone 2-phenyl semicarbazone there is formed methylene phenylhydrazone, $CH_2{=}NNHC_6H_5$, which combines immediately in molecular proportion with unchanged acetone 2-phenyl semicarbazone in accordance with the equation: $C_{10}H_{13}ON_3 + C_7H_8N_2 = C_{17}H_{21}ON_5$.

This view is supported mainly through the behavior of Product A towards acids. Although stable in alkaline media, it is readily decomposed by even weak acids, such as oxalic acid. In reaction with one mole of a dilute acid it yields among other substances 2-phenyl semicarbazide and acetone in molecular proportions. This indicates that in the preparation of Product A one-half of the acetone-2-phenyl semicarbazone employed enters the new compound unoxidized and in the disintegration of Product A is reformed with subsequent hydrolysis to acetone and 2-phenyl semicarbazide, Furthermore, when an excess of acid is used in the decomposition, phenylhydrazine, carbon dioxide and ammonia are formed instead of 2-phenyl semicarbazide. The formation of the above products is in accord with the behavior of 2-phenyl semicarbazide on acid hydrolysis.[9] It seems certain, therefore, that in the formation of Product A there are involved one molecule of acetone 2-phenyl semicarbazone and one molecule of a product of the formula, $C_7H_8N_2$.

Further structural proof is afforded by the fact that in the acid decomposition not only is there formed the hydrolysis product of acetone

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[8] Goodwin and Bailey, THIS JOURNAL, **47, 169 (1925).**

[9] Goodwin **and Bailey,** *ibid.*, **46, 2831 (1924).**

2-phenyl semicarbazone, referred to above, but an amount of nitrogen gas corresponding to two-fifths of that contained in a substance of the formula, $C_{17}H_{21}ON_5$, is liberated. There also results a large amount of benzene along with an appreciable amount of diphenyl. It is quite evident that the nitrogen, benzene and diphenyl have their origin in that part of Product A represented by the complex $C_7H_8N_2$.

Only two structures appear available for $C_7H_8N_2$, to wit, (1) $CH_2{=}NNHC_6H_5$ and (2) $CH_3N{=}NC_6H_5$, that is, methylene phenylhydrazone and phenylazomethane, respectively. However, were the assumption made that nitrogen, benzene and diphenyl result from either of these products on acid hydrolysis, it would not be in accord with the chemical behavior of compounds of either type. A substance of structure (1) would be expected to undergo simple hydrolysis to formaldehyde and phenylhydrazine, and a substance of structure (2) should be comparatively stable toward acid hydrolysis.

Either methylene phenylhydrazone or phenylazomethane might conceivably result from the oxidation of acetone 2-phenyl semicarbazone, but the former rather than the latter seems the more likely choice for the following reasons. Methylene phenylhydrazone has not as yet been isolated in the monomolecular form for a certainty.[10] Its pronounced property of polymerization would indicate a probable strong tendency to react under favorable conditions at the moment of formation. Phenylazomethane is known, and its properties have been studied, but as yet no additive reactions of this substance have been observed. This is in accord with the non-reactivity in general of azo bodies. A limited number of azo compounds, in particular diethyl azocarbonate, $C_2H_5OOCN{=}NCOOC_2H_5$,[11] show additive reactions, but only in special cases, where strongly electronegative radicals are attached to the azo group, has such a behavior been reported. All efforts in the course of this investigation to effect a reaction between phenylazomethane and acetone 2-phenyl semicarbazone in an alkaline medium in the hope of synthesizing Product A have met with only negative results. Furthermore, we have found diethyl azocarbonate non-reactive toward acetone 2-phenyl semicarbazone.

The possibility of synthesizing Product A by the action of formaldehyde upon an equimolecular mixture of phenylhydrazine and acetone 2-phenyl semicarbazone suggested itself, but here again all experiments were fruitless.

In a further attempt to clarify the mechanism of the reactions involved in the formation of Product A, a very simple method of preparation of tetrazones from ketone phenyl hydrazones was discovered. Although acetone phenyl hydrazone is not oxidized by amyl nitrite under the conditions employed by von Pechmann for aldehyde phenylhydrazones, it is con-

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[10] Ref. 9, p. 168.

[11] Diels and Fritzsche, *Ber.*, 44, 3018 (1911).

verted in almost quantitative yield to the hitherto unknown dipropylidenediphenyldihydrotetrazone, $(CH_3)_2C{=}N{-}N(C_6H_5)N(C_6H_5)N{=}C(CH_3)_2$, by the action of potassium permanganate in acetone solution. This reaction was extended to the phenylhydrazone of methylethyl ketone, although the tetrazone formed here has been obtained only as a yellow, viscous oil and was not analyzed.

In connection with the oxidation of acetone 2-phenyl semicarbazone, it may be pointed out that the behavior of acetone phenylhydrazone toward permanganate in acetone solution, as reported above, excludes the assumption of this latter hydrazone as an intermediary product in the formation of Product **A.** This leads to the conclusion that there is first formed methylene 2-phenyl semicarbazone, $CH_2{=}NN(CONH_2)C_6H_5$, from which the carbamyl group is hydrolyzed either before or after addition to unchanged acetone 2-phenyl semicarbazone. It was impossible, however, to submit this view to experimental proof due to the fact that conditions for the formation of methylene 2-phenyl semicarbazone have not been established.

Based on the assumption that Product A results from the union of one mole of methylene phenylhydrazone with one mole of acetone 2-phenyl semicarbazone, experiments were instituted to determine whether certain well-known phenylhydrazones, such as acetaldehyde phenylhydrazone and acetone phenylhydrazone would show a reactivity toward acetone 2-phenyl semicarbazone. It was found that beautiful, yellow products result here when potassium hydroxide is used as a catalyst, but unfortunately the analytical data on the substances isolated did not conform to the expected formulas, so this phase of the investigation has not been concluded. However, the results achieved apparently strengthen the views advanced on the mechanism of the permanganate oxidation of 2-phenyl semicarbazone.

As regards the structure of Product A, two formulas are suggested:

VI. $(CH_3)_2CH(C_6H_5N{=}NCH_2)N{-}N(C_6H_5)CONH_2$ and
VII. $C_6H_5N{=}NCH_2C(CH_3)_2NHN(C_6H_5)CONH_2$

Both formulas indicate that Product A is not of hydrazone structure, an interpretation that conforms to its non-reactivity with benzaldehyde. Were the complex $(CH_3)_2C{=}N$ present in acetone 2-phenyl semicarbazone, still intact in its oxidation product, we might expect, as is so often the case, that the propylidene group could be substituted by the benzal group. For two reasons Formula VI is given preference over VII: (1) no evidence has been found of the presence of an imino group in Product A; (2) on acid decomposition of a product of structure VII the formation of acetone would not be expected. Formula VI is not open to these objections and, accordingly, Product A is most probably 1-*iso*propyl-1-phenylazomethyl-2-phenyl semicarbazide.

A confirmation of the interpretation advanced for the oxidation of acetone 2-phenyl semicarbazone is furnished by the oxidation of methylethyl ketone 2-phenyl semicarbazone, where there results a beautifully crystallizing, yellow compound with properties analogous in every way to those of Product A. It has the formula $C_{18}H_{23}ON_5$, which is the equivalent of one molecule of the original semicarbazone plus one molecule of methylene phenylhydrazone. This formula was confirmed by molecular weight determination, this substance being selected in preference to Product A because of its greater solubility in benzene.

As was to be expected, it was found that benzal 2-phenyl semicarbazone, where the formation of methylene phenylhydrazone is excluded, was not acted on by permanganate in acetone solution. The ethyl ester of pyruvic acid 2-phenyl semicarbazone was also not acted on by permanganate under similar conditions. However, pyruvic acid 2-phenyl semicarbazone in contrast to its ester is readily attacked by this oxidizing agent, but the reaction product was not isolated. Acetaldehyde 2-phenyl semicarbazone undergoes oxidation with permanganate in acetone solution very readily; here the problem is complicated by the possible formation of diacetyl-2-phenyl semicarbazone, $C_6H_5N(CONH_2)N{=}C(CH_3)C(CH_3){=}NN(CONH_2)C_6H_5$, and no definite oxidation products were isolated.

With the view of studying its behavior toward permanganate, acetone 2,4-diphenyl semicarbazone, $C_6H_5N(CONHC_6H_5)N{=}C(CH_3)_2$, was prepared by the action of phenylisocyanate on acetone phenylhydrazone, but in the oxidation experiment no definite result was obtained.

Although benzal-2-phenyl semicarbazone is not attacked in the permanganate oxidation in acetone solution, it behaves analogously to benzal semicarbazone, in its conversion to 3-hydroxy-2,5-diphenyltriazole on oxidation with ferric chloride.[12]

Experimental Part

Oxidation of Acetone 2-Phenyl Semicarbazone.—To 100 g. of crude acetone 2-phenyl semicarbazone[13] in 500 cc. of acetone is slowly added 125 g. of potassium permanganate, partially dissolved in acetone. The oxidation proceeds rapidly with considerable rise in temperature and after twelve hours the permanganate is completely reduced. The reaction product, designated as Product A, which is formed in a yield of about 64 g. and imparts a bright yellow color to the acetone, remains in solution for the most part but separates on concentration of the filtered solution or can be precipitated by the addition of an equal volume of water. Any of the substance remaining in the cake after filtration can be extracted with boiling acetone or alcohol. It is readily soluble in alcohol, benzene, acetone and acetic ether, less soluble in ether, and practically insoluble in water. Recrystallized from alcohol, it separates in fine, canary-yellow needles melting at 162° with violent gas evolution.

Anal. Calcd. for $C_{17}H_{21}ON_5$: C, 65.59; H, 6.75; N, 22.54. Found: C, 65.34; H, 6.76; N, 22.95.

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[12] Young and Witham, J. *Chem. Soc.*, 77, 226 (1900).

[13] Ref. 9, p. 2829.

Decomposition of Product A on Acid Treatment.—To 10 g. of Product A in a round-bottomed flask, connected to a condenser fed with ice water, is added 67 cc. of $N/2$ hydrochloric acid. As soon as the receiver is thoroughly chilled by immersion in a freezing mixture, the flask is heated with a low, smoky flame, whereupon a reaction with profuse evolution of nitrogen takes place. After half an hour the reaction map be considered at an end. The distillate, measuring about 4.5 cc., consists of a mixture of acetone and benzene, while in the flask there remain 2-phenyl semicarbazide in solution and in addition a small amount of insoluble tar from which can be isolated diphenyl. The methods of isolation and detection of the different decomposition products follow.

Identification of Acetone and Benzene.—The distillate obtained from the above reaction was fractionated at atmospheric pressure, four fractions boiling at 50–65°, 65–70°, 70–75° and 75–80", respectively, being collected. In the lower boiling fractions acetone predominated, while the higher boiling fractions were rich in benzene. Only the last fraction solidified when chilled in ice water. The first fraction was treated with benzaldehyde in alcoholic sodium hydroxide solution,[14] and the dibenzylidene acetone formed identified by analysis and comparison with a stock sample.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.18; H, 5.98. Found: C, 87.33; H, 5.88.

In order to confirm the formation of benzene, the last fraction was treated with a mixture of nitric and sulfuric acids as directed bv Mulliken,[15] and the *m*-dinitrobenzene formed identified by a nitrogen determination and comparison with a stock sample.

Anal. Calcd. for $C_6H_4O_4N_2$: N, 16.67. Found: N, 16.71.

Identification of 2-Phenyl Semicarbazide.—In the course of the investigation it was found that pyruvic acid 2-phenyl semicarbazone is admirably suited for the characterization of 2-phenyl semicarbazide. The acid solution remaining in the distillation flask after the decomposition of Product A with hydrochloric acid was concentrated to a small volume and, after the addition of an excess of sodium acetate, a little more than the calculated amount of pyruvic acid was added. This product was compared in the usual way with a sample of the semicarbazone prepared, as described later on, from 2-phenyl sernicarbazide hydrochloride and pyruvic acid.

Anal. Calcd. for $C_{10}H_{11}O_3N_3$: N, 19.00. Found: N, 18.92.

Identification of Diphenyl.—The residual tar from the decomposition of Product A yielded on distillation in a vacuum a beautifully crystallizing, white solid. This was identified as diphenyl by its characteristic odor, by the usual comparison with a stock sample and finally by the intense blue coloration it developed in chloroform solution with sublimed aluminum chloride.[16]

Estimation of the Acetone Formed in the Decomposition of Product A.—The acetone from the decomposition of 0.216 g. of Product A with $N/2$ sulfuric acid was distilled off and converted to iodoform;[17] 22.9 cc. of $N/10$ iodine solution was used, corresponding to 0.0442 g. of acetone. The calculated amount of acetone furnished in the decomposition of 0.2161 g. of Product A equals 0.0403 g.

Estimation of the Nitrogen Evolved in the Decomposition of Product A.—One gram of Product A was decomposed with 7 cc. of $N/2$ hydrochloric acid, as described above, in an atmosphere of carbon dioxide, and the gas evolved collected over 30% potassium hydroxide solution. The gas volume measured 77.1 cc. at 21° and 754 mm., corresponding to 40% of the total nitrogen in the original substance.

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[14] Mulliken, "Identification of Pure Organic Compounds," 1st ed., John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 148.

[15] Ref. 14, p. 200.

[16] Ref. 14, p. 196.

[17] See Ullman, "Enzyklopadie der technischen Chemie," 1914, Vol. I, p. 112.

Pyruvic Acid 2-Phenyl Semicarbazone.—When to 6 g. of 2-phenyl semicarbazide hydrochloride in 20 cc. of water 8 g. of fused sodium acetate and 3.4 g. of pyruvic acid are added, there separates a fine, crystalline reaction product, difficultly soluble in all the common solvents. It can be purified by recrystallization from water and is thus obtained in the form of microscopic cubes melting with decomposition at 168°.

Anal. Calcd. for $C_{10}H_{11}O_3N_3$: N, 19.00. Found: N, 18.90.

The Ethyl Ester of Pyruvic Acid 2-Phenyl Semicarbazone.—Prepared similarly to the free acid by using pyruvic acid ester, this semicarbazone is obtained in a practically quantitative yield. It is readily soluble in alcohol, benzene and acetic ether and practically insoluble in water and can be purified by recrystallization from alcohol in the form of long rods melting at 149°. Unlike the free acid, the semicarbazone ester is quite stable toward permanganate in acetone solution.

Anal. Calcd. for $C_{12}H_{15}O_3N_3$: N, 16.87. Found: N, 17.02.

Oxidation of Methylethyl Ketone 2-Phenyl Semicarbazone.—This semicarbazone[18] can be conveniently obtained by the method, previously referred to, that Goodwin and Bailey used in the case of acetone 2-phenyl semicarbazone. In its oxidation the following procedure will be found satisfactory: 8 g. of the semicarbazone is added to 100 cc. of acetone, in which is dissolved or suspended 25 g. of potassium permanganate, and the reaction mixture allowed to stand with occasional agitation for one week. Precipitation of the new substance is then effected by addition of water to the filtered solution. The crude product, in order to destroy any unchanged permanganate, is dissolved in boiling alcohol, from which on dilution to a permanent turbidity and chilling, it separates as a fine, granular, yellow solid melting at 144° with gas evolution. The new substance is extremely soluble in acetone, alcohol and benzene, less soluble in ether and practically insoluble in water. On treatment with acids this oxidation product decomposes in a way similar to Product A.

Anal. Calcd. for $C_{18}H_{23}ON_5$: C, 66.46; H, 7.08; N, 21.54. Found: C, 66.54; H, 7.33; N, 21.78. *Molecular weight determination.* 0.6634 of substance in 40.8 g. of benzene gave a boiling point elevation of 0.130°, and 0.4928 g. substance in 52.3 g. of benzene gave an elevation of 0.066'. Calcd. for $C_{18}H_{23}ON_5$: M. W., 325. Found: M. W., 313, 347.

Dipropylidene Diphenyl Tetrazone.—To 60 g. of acetone phenylhydrazone in 300 cc. of acetone, cooled in ice water, powdered potassium permanganate is slowly added until a permanent pink color persists, care being taken to avoid an elevation of temperature. A part of the tetrazone, which separates with the manganese dioxide, is extracted with hot acetone. From the combined acetone solutions, on dilution with two volumes of water and chilling, the tetrazone precipitates in a yield of 85% of that calculated. It is very soluble in alcohol, acetone and ether, insoluble in water, and can be purified by recrystallization from 95% alcohol, care being taken not to heat the solution longer than necessary. It crystallizes in thin, yellow plates melting at 89° undecomposed.

Anal. Calcd. for $C_{13}H_{22}N_4$: C, 73.47; H, 7.48; N, 19.04. Found: C, 73.81; H, 7.37; N, 18.98

Action of Alcohol on the Tetrazone.—When the tetrazone is refluxed with a large excess of alcohol for an hour, and the alcohol then distilled off, there remains a slightly colored, rather mobile liquid. This was identified as acetone phenylhydrazone by its boiling point, by conversion to 2-phenyl semicarbazone and by a nitrogen determination.

Anal. Calcd. for $C_9H_{12}N_2$: N, 18.92. Found: N, 18.74.

Action of Acids on the Tetrazone.—If 2 g. of the tetrazone in 25.5 cc. of *N*/2 hydro-

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[18] Arnold, *Ber.*, 30, 1016 (1897).

chloric acid is heated for ten minutes, complete solution is effected and acetone distils off. On concentration of the solution to a small volume, phenylhydrazine hydrochloride crystallizes out in the form of white, lustrous flakes. This was identified by comparison with a stock sample as well as by conversion to benzal phenylhydrazone.

Behavior **of the Tetrazone** toward **Pyruvic** Acid.—Pyruvic acid reacts in the cold with the tetrazone suspended in water, effecting at first complete solution followed later by precipitation of pyruvic acid phenylhydrazone. The hydrazone was identified by comparison in the usual way with a sample prepared from phenylhydrazine and pyruvic acid.

3-Hydroxy-2,5-diphenyltriazole.—Although benzal 2-phenyl semicarbazone is quite stable toward permanganate in acetone solution, it is oxidized to the corresponding triazole as follows: 1.5 g. of benzal 2-phenyl sernicarbazone, 1.5 g. of ferric chloride and 10 cc. of alcohol are heated in a sealed tube at 125–135° for three hours. Only a slight pressure is developed and at the end of the reaction the contents of the tube solidify. For purification the triazole is dissolved in dilute sodium hydroxide and after filtration reprecipitated with hydrochloric acid. It is readily soluble in alcohol, acetic ether and glacial acetic acid, difficultly soluble in chloroform and ether, and can be recrystallized from absolute alcohol in a matted mass of very fine, hair-like needles melting at 233°.

Anal. Calcd. for $C_{14}H_{11}ON_3$: N, 17.73. Found: N, 17.22.

Acetone 2,4-**Diphenyl Semicarbazone.**—When acetone phenylhydrazone and phenylisocyanate in molecular proportions are heated without a solvent at 100° in a sealed tube for two hours, a viscous reaction product results. This, purified by recrystallization from alcohol in the form of thin plates, melts at 191° and is readily soluble in-alcohol, benzene and chloroform, difficultly soluble in ether and insoluble in water The substance, prepared with a view of observing its behavior towards oxidizing agents, was found in contrast to acetone-2-phenyl semicarbazone to be quite stable toward permanganate in acetone solution.

Anal. Calcd. for $C_{16}H_{17}ON_3$: N, 15.73. Found. 15.68.

Summary

1. Acetone 2-phenyl semicarbazone, $(CH_3)_2C{=}NN(CONH_2)C_6H_5$, on oxidation in acetone solution with potassium permanganate gives a yellow product regarded as 1-*iso*propyl-1-phenylazomethyl-2-phenyl semicarbazide, $(CH_3)_2CH(C_6H_5N{=}NCH_2)N{-}N(C_6H_5)CONH_2$.

2. The behavior of this oxidation product indicates its formation from one mole of unchanged acetone-2-phenyl semicarbazone and one mole of methylene phenylhydrazone. A direct synthesis of the substance from these two products, however, has not been accomplished.

3. Methylethyl ketone 2-phenyl semicarbazone behaves similarly on oxidation, yielding a yellow product regarded as 1-*sec.*-butyl-1-phenylazomethyl-2-phenylsemicarbazide. It is probable that all aliphatic ketone semicarbazones of the formula, $R'R''C{=}NN(C_6H_5)CONH_2$, will yield as primary oxidation product the complex, $C_7H_8N_2$, which in reaction with the original unchanged 2-phenyl semicarbazone will produce semicarbazides of the type, $R'R''CH(C_6H_5N{=}NCH_2)NN(C_6H_5)CONH_2$.

4. In the course of the investigation a convenient method of preparation of tetrazones by the oxidation of ketone phenylhydrazones with permanganate in acetone solution was discovered.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

THE MECHANISM UNDERLYING THE REACTION BETWEEN ALDEHYDES OR KETONES AND TAUTOMERIC SUBSTANCES OF THE KETO-ENOL TYPE

II. THE CONDENSATION OF OXOMALONIC ESTER WITH CYANO-ACETIC AND MALONIC ESTERS

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Various mechanisms have been proposed for the reaction between carbonyl compounds and substances containing active hydrogen. Among these is the suggestion that aldol condensation is preceded by and is dependent upon preliminary enolization of the carbonyl compound.[1]

On this basis, the well-known ease with which benzaldehyde (a substance incapable of enolization) condenses with cyano-acetic ester, malonic ester and other substances containing active hydrogen, has been explained[2] by a sort of pseudo-enolization resulting in a tautomeric form containing bivalent carbon, $C_6H_5—\overset{|}{\underset{|}{C}}—OH$.

The inability of benzophenone to condense has been advanced as an argument for this mechanism of preliminary enolization. It is true that benzophenone cannot enolize and that it does not undergo condensation reactions, but these two facts need not be related as cause and effect. If the mechanism of condensation between aldehydes or ketones and substances containing active hydrogen is assumed to be, first, 1–2 addition to the carbonyl group—equivalent to aldol condensation—and, second, elimination of water from the addition product, then the reactivity of a carbonyl compound in condensation would run parallel with its reactivity in other addition reactions and one would predict from the sluggishness of benzophenone toward addition reactions[3] in general that benzophenone would undergo condensation with great difficulty, if at all. Thus it would be a mere coincidence that benzophenone is at the same time unable to enolize and also to condense.

Inasmuch as there are carbonyl compounds that are incapable of enolization and yet undergo addition reactions readily, it is possible to determine definitely whether enolization is involved in these condensations or not. The two most promising substances for this purpose are the esters of benzoylformic and oxomalonic acids. In a previous paper[4] it was shown

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[1] (a) Rogerson and Thorpe, J. *Chem. Soc.*, 87,1685 (1905); (b) Harding, Haworth and Perkin, *ibid.*, 93, 1943 (1908); (c) Haworth, ibid., 95, 480 (1909).

[2] Ingold, *ibid.*, 119, 329 (1921).

[3] (a) Stewart, *ibid.*, 87, 185 (1905); (b) Petrenko-Kritschenko, Ann., 341, 150 (1905).

[4] Kohler and Corson, THIS JOURNAL, 45, 1975 (1923).

that the esters of benzoylformic acid condense with cyano-acetic and malonic esters with extraordinary ease; this paper deals with the corresponding reactions of oxomalonic ester.

The condensation of oxomalonic ester with cyano-acetic ester has already been studied by Schmitt[5] but he did not succeed in establishing the structure of any of his products. We have repeated his experiments and have established the structure of his principal product. The reaction proceeds as he assumed.

$$CO(CO_2C_2H_5)_2 + 2CH_2(CN)CO_2CH_3 \longrightarrow \underset{\mathrm{I}}{(CO_2C_2H_5)_2C[CH(CN)CO_2CH_3]_2}$$

By hydrolysis and subsequent loss of carbon dioxide the product was converted into tricarballylic acid.

$$\underset{\mathrm{I}}{(CO_2C_2H_5)_2C[CH(CN)CO_2CH_3]_2} \longrightarrow \underset{\mathrm{II}}{CH_2CO_2HCHCO_2HCH_2CO_2H}$$

Besides repeating Schmitt's experiments with cyano-acetic ester, we also condensed malonic ester with oxomalonic ester. This condensation is more significant because here we were able to isolate an intermediate compound which could be formed only by the addition of malonic ester to the carbonyl group of the oxo compound.

$$(CH_3O_2C)_2CO + CH_2(CO_2CH_3)_2 \longrightarrow \underset{\mathrm{III}}{(CH_3O_2C)_2COHCH(CO_2CH_3)_2}$$

The elements of water were eliminated from the hydroxy compound to form an unsaturated ester.

$$\underset{\mathrm{III}}{(CH_3O_2C)_2COHCH(CO_2CH_3)_2} \longrightarrow \underset{\mathrm{IV}}{(CH_3O_2C)_2C{:}C(CO_2CH_3)_2} + H_2O$$

This unsaturated compound was also obtained as the direct condensation product of the two original esters.

The unsaturated compound was reduced to the saturated ester, which in turn was hydrolyzed to the corresponding tetrabasic acid. The resulting acid decomposed on heating and formed succinic acid.

$$\begin{tikzcd}
\underset{\mathrm{V}}{(C_2H_5O_2C)_2C{:}C(CO_2C_2H_5)_2} \arrow[r] & \underset{\mathrm{VI}}{(C_2H_5O_2C)_2CHCH(CO_2C_2H_5)_2} \arrow[d] \\
HO_2CCH_2CH_2CO_2H & \underset{\mathrm{VII}}{(HO_2C)_2CHCH(CO_2H)_2} \arrow[l]
\end{tikzcd}$$

Our results show that a substance which is incapable of enolization undergoes condensation readily. Therefore, there is no reason for assuming that aldol (or ketol) condensation involves enolization of the carbonyl compound as a preliminary step.

Experimental Part

I. Condensation of Oxomalonic Ester with Cyano-acetic Ester

Tetramethyl 1,3-Dicyano-propane-1,2,2,3-tetracarboxylate, VIII.—Thirty-seven g. of dimethyl oxomalonate was added to 55 g. of methyl cyano-acetate and to the mixture

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[5] Schmitt, Ann. *chim.*, [8] 12, 411 (1907).

were added, with shaking, 30 drops of piperidine. The mixture became warm and darkened. It was heated under a calcium chloride tube on a steam-bath for two hours. At the end of two hours[6] drops of water could be seen floating in the oil, thus showing that reaction had taken place. On cooling and filtering (sometimes it was necessary to add some alcohol in order to induce crystallization), 20 g. of the substance in question was obtained (25% of the theoretical amount). It was crystallized from methyl alcohol; it also crystallizes nicely from dilute acetic acid. It is very soluble in acetone; less soluble in alcohol, chloroform, benzene; sparingly soluble in ether; insoluble in toluene and petroleum ether. It melts at 118–120°.[7] Schmitt gave the melting point as 120".

Anal. Calcd. for $C_{13}H_{14}O_8N_2$: N, 8.6. Found: N, 8.9.

Molecular Weight. Calcd. for $C_{13}H_{14}O_8N_2$: 326. Found, in freezing acetic acid: 324.

Dimethyldiethyl 1,3-Dicyano-propane-1,3,2,2-tetracarboxylate, I.—This substance was obtained by the same procedure. The yield was somewhat better—42% of the theoretical amount. It melts at 114–115°. Schmitt gave 103° as the melting point.

Anal. Calcd. for $C_{15}H_{18}O_8N_2$: C, 50.9; H, 5.1; N, 7.9. Found: C, 51.4, 51.2; H, 5.1, 5.1; N, 8.0.

Molecular Weight. Calcd. for $C_{15}H_{18}O_8N_2$: 354. Found, in freezing acetic acid: 333, 369.

Ineffectual Attempt to Obtain Triethylcyano-ethylenetricarboxylate, $(C_2H_5O_2C)_2$-C: $C(CN)CO_2C_2H_5$.[5]—At first we followed Schmitt's directions, using piperidine as catalyst, but we were unable to duplicate his results.

We next used a zinc chloride catalyst.[8] This catalyst gave good results in the condensation of malonic ester but it was not very successful with cyano-acetic ester. We did, however, obtain a small amount of liquid which distilled around 170° at 5 mm. and which solidified to a waxy solid after cooling for several hours. It gave figures for molecular weight which could be applied to the cyano-ester, but Kjeldahl analysis showed but 3% of nitrogen whereas the formula for triethylcyano-ethylenetricarboxylate calls for 5.2%. We did not investigate this product further hut considered it a mixture of tetra-ethylethylenetetracarboxylate (V) and triethylcyano-ethylenetricarboxylate. In several of the runs we were able to isolate small amounts of tetra-ethylethylenetetracarboxylate. This product must have been due to an impurity of ethyl malonate in our ethyl cyano-acetate.

Finally, we tried the following procedure which had been found to give good results with malonic ester. We mixed oxomalonic ester with cyano-acetic ester and added piperidine. The mixture was allowed to stand for fifteen minutes at room temperature and finally for one hour in the ice-bath. We then poured the mixture into cold, concentrated sulfuric acid, allowed the solution to stand for thirty minutes and finally poured it into water. We tried this procedure on both the methyl and ethyl esters but the only product we could isolate was the tetra ester in very small yield.

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[6] Schmitt obtained this substance and the one described below, but **only** after allowing the reaction to run for three weeks or so..

[7] All melting points are corrected for exposed stem and were read from a thermometer which had been calibrated against a thermometer tested by the U. S. Bureau of Standards.

[8] This catalyst was prepared by adding 100 g. of anhydrous zinc chloride to 200 g. of acetic anhydride and shaking the mixture on a shaking machine for about four hours. The greater part of the zinc chloride dissolved. The solution should be used while fresh since it becomes viscous and dark on standing.

II. Proof of the Structure of Condensation Product I

We were unable to esterify the nitrile groups in the tetramethyl dicyano ester (I) to form the corresponding hexamethyl ester,[9] but the structure of the substance was finally established by its hydrolysis and decarboxylation to tricarballylic acid (II).

Hydrolysis and Decarboxylation with Hydrochloric Acid.—Twenty g. of the ester was gently refluxed for nine hours with 200 cc. of 20% hydrochloric acid in the apparatus described by Clarke[10] for the preparation of tricarballylic acid. The solution was then heated by means of a boiling water-bath and evaporated to dryness in a vacuum. Dry air was slowly aspirated through the flask to remove the last traces of hydrochloric acid. Finally, the mixture of ammonium chloride and tricarballylic acid was dissolved in water and the solution treated with Norit. After filtering, the solution was evaporated to dryness in a vacuum. The solid was thoroughly dried by the slow aspiration of dry air through the flask and was finally extracted with acetone. The solid obtained by evaporating the acetone was washed with ether. It weighed 6.5 g., which corresponds to a quantitative yield of tricarballylic acid. The solid melted at 153–157°.

Purification of the Tricarballylic Acid Obtained by Hydrolysis.—Tricarballylic acid is difficult to recrystallize in small amounts. We tried dry ether[10] without success. Eventually, we found a method which could be applied to our crude acid. The product was dissolved in 30 cc. of acetone and to the solution was added an equal volume of benzene. The solution was heated on a steam-bath and about half of the solvent was evaporated. On cooling, the product crystallized pure and in good yield. It melted at 159–160° and was completely identified by comparison with a specimen of tricarballylic acid.[10]

III. Condensation of Oxomalonic Ester with Malonic Ester

Tetramethyl 1-Hydroxy-ethane-1,1,2,2-tetracarboxylate, 111.—This was the only addition product we were able to isolate. Nine g. of dimethyl oxomalonate was added to 6.5 g. of dimethyl malonate and to the mixture was added 20 drops of piperidine. The mixture darkened and became hot. On cooling in ice the liquid quickly solidified. The product weighed 7 g. (50% of the theoretical amount) after crystallizing from methyl alcohol. Usually aldols are so prone to reverse to the original components that it is advisable to acidify slightly the solvent used in crystallization with a few drops of acetic acid in order to neutralize any traces of the alkaline catalyst which might be present. However, this aldol seemed quite stable and was recovered in good yield on crystallization from ordinary methyl alcohol. It melts at 87.5–88.5°. It is very soluble in acetone; less soluble in methyl alcohol, ether, benzene and water; insoluble in petroleum ether. It crystallizes nicely from alcohol, ether or benzene.

Anal. Calcd. for $C_{10}H_{14}O_9$: C, 43.2; H, 5.0. Found: C, 43.1; H, 4.9.

Molecular Weight. Calcd. for $C_{10}H_{14}O_9$: 278. Found, in boiling acetone: 291.

Removal of Elements of Water from Aldol.—The first dehydrating agent tried was one which often gives good results with aldols,[4] namely, glacial acetic acid. For this purpose 1.3 g. of the hydroxy compound was warmed on a steam-bath for one hour with 5 cc. of acetic acid; the solution was then poured into water. No solid was deposited. However, a 40% yield resulted through the action of concentrated sulfuric acid. Two g. of aldol was dissolved in 10 cc. of cold, concentrated sulfuric acid and the solution allowed to stand for twenty-five minutes at room temperature. On pouring into 300 cc. of water, 0.7 g. of the unsaturated product quickly crystallized. Dilute

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[9] Bischoff, Ber., 29, 1279, 1746 (1896).

[10] Clarke and Murray, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. IV, p. 77.

sulfuric acid, corresponding to 10 cc. of concentrated acid in 300 cc. of water, did not bring about dehydration. Neither was the unsaturated product obtained by adding molecular equivalents of oxomalonic and malonic esters to concentrated sulfuric acid, allowing the solution to stand for twenty-five minutes and then pouring into 300 cc. of water. Therefore, the unsaturated product was formed by the dehydration of the hydroxy compound and not from the original components into which the aldol might have been reversed during contact with the concentrated sulfuric acid.

Dehydration did not take place when an alcoholic solution of the aldol was treated with piperidine and allowed to stand for several days at room temperature nor when the solution was refluxed for several hours. Sodium alcoholate hydrolyzed the ester groups and yielded a sodium salt which we did not investigate.

Tetra-ethyl 1-Hydroxy-ethane-1,1,2,2-tetracarboxylate, $(C_2H_5O_2C)_2COHCH(CO_2C_2H_5)_2$.—This substance could not be isolated in pure condition since it is a liquid which cannot be distilled. It was prepared in the same way as the tetramethyl ester (III). It was obtained as a yellow, viscous liquid which reversed to the original components when subjected to vacuum distillation. Molecular weight determination in boiling acetone gave figures which could be applied equally well to the hydroxy compound or to the unsaturated ester. However, it seemed that it must be the hydroxy compound since the unsaturated ester distils nicely in a vacuum. We were unable to acetylate this product but we did obtain from it good yields of the unsaturated ester by the dehydrating action of concentrated sulfuric acid.

Eleven g. of diethyl oxomalonate was mixed with 8 g. of diethyl malonate and to the mixture was added 20 drops of piperidiie. The temperature of the mixture quickly rose to 90°.[11] After standing at room temperature for fifteen minutes it was cooled[12] in ice for an hour. The thick, yellow liquid was poured into 50 cc. of cold, concentrated sulfuric acid and the solution allowed to stand for thirty minutes at room temperature. This solution was then poured with stirring into 500 cc. of water. On standing for twelve hours, 8 g. of the unsaturated ester (V) was obtained (50% of the theoretical amount). It was also established that sulfuric acid under the conditions of the experiment did not bring about condensation between ethyl oxomalonate and ethyl malonate.

Tetra-ethyl Ethylenetetracarboxylate, V.—A mixture of 66 cc. of ethyl oxomalonate, 50 cc. of ethyl malonate and 145 cc. of zinc chloride-acetic anhydride catalyst was heated in a boiling water-bath for one hour under a reflux condenser protected by calcium chloride. The mixture was then poured into 500 cc. of water and allowed to stand for twelve hours with occasional stirring. A more or less dark solid was deposited. The mixture was extracted with three portions of ether. The ethereal solution was washed several times with water to remove zinc chloride, then with sodium carbonate solution to neutralize the acetic acid and finally with water. It was then warmed with Norit, filtered and dried with calcium chloride. After distilling the ether the solid was crystallized from ethyl alcohol. The yield was 79 g. or 80% of the theoretical amount. It melts at 54.5–56.5°.

Molecular Weight. Calcd. for $C_{14}H_{20}O_8$: 316. Found, in boiling acetone: *322*, 290; in freezing acetic acid: 306.

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[11] This rise in temperature is no indication that condensation has taken place between the two esters since a heating effect is observed when piperidine is added to oxomdonic ester alone.

[12] Koelichen [*Z. physik. Chem.*, 33, 129 (1900)], in his study of the kinetics of the condensation of acetone to diacetone alcohol, showed that low temperature forced equilibrium in the direction of the addition product. Low temperature has the same effect in this condensation and also in the reaction between methyl benzoylformate and methyl cyano-acetate.

It was identified as tetra-ethyl ethylenetetracarboxylate by mixed melting point comparison with a sample prepared according to the directions of Blank and Samson.[13]

Tetramethyl Ethylenetetracarboxylate, IV.—This substance was obtained by condensing dimethyl oxomalonate with dimethyl malonate in the presence of a solution of zinc chloride in acetic anhydride. In this condensation and in the one above an excess of oxomalonate is preferable to an excess of malonate since the former is removed during extraction due to its solubility in water. Since the tetramethyl ester is not very soluble in ether the greater part of the yield was obtained by filtering off the solid rather than by ether extraction. The yield was 51% of the theoretical amount. It melts at 119–120°. This substance was identical with the product obtained by removing the elements of water from hydroxy compound III.

Molecular Weight. Calcd. for $C_{10}H_{12}O_8$: 260. Found, in boiling acetone: 240, 265.

Its identity was proved by a mixed melting point comparison with a sample of tetramethyl ethylenetetracarboxylate.

IV. Proof of the Structure of the Condensation Products

Our formula for the addition product (III) is based on the method by which it is obtained and on its relation to the unsaturated ester (IV) which is formed from it by the elimination of water. Although the unsaturated condensation product proved identical with ethylenetetracarboxylate as prepared by the method of Blank and Samson, we thought it advisable to relate its structure directly to that of succinic acid, since bromomalonic ester is capable of yielding various products with only slight changes in manipulation. We therefore reduced it to the corresponding saturated ester (VI), hydrolyzed this and decomposed the resulting acid (VII). The product was succinic acid.

This work was aided by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.

Summary

1. In the presence of a small quantity of piperidine, oxomalonic ester condenses with malonic ester as follows.

$$(RO_2C)_2CO + CH_2(CO_2R)_2 \longrightarrow (RO_2C)_2COHCH(CO_2R)_2$$

2. With zinc chloride-acetic anhydride as catalyst, oxomalonic ester reacts with malonic ester to form the corresponding unsaturated ester, which can also be formed by eliminating water from the addition product.

3. With piperidine as catalyst, oxomalonic ester reacts with 2 equivalents of cyano-acetic ester to produce compounds of type $(CO_2R)_2C[CH(CN)CO_2R]_2$.

4. It seems certain that enolization of aldehydes or ketones is not involved in the reaction between aldehydes or ketones and substances containing active hydrogen.

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[13] Blank and Samson, *Ber.*, 32,860 (1899).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. IV

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When two acyl groups are introduced into o-aminophenol, and then the order of introduction is reversed, identical products are usually obtained, or the product may be an equilibrium mixture of the two isomeric di-acyl derivatives.

The literature on this subject may be reviewed by referring to the work of Ransom,[1] Ransom and Nelson,[2] Nelson and co-workers[3] and Raiford with co-workers.[4]

The evidence of previous work indicates that both the weight and acidity of the acyl groups are factors in determining which acyl group attaches to the nitrogen. While the heavier group, in many cases, attaches itself to the nitrogen, there are definite exceptions to this. The more acidic group would be expected to attach itself to the nitrogen, but Raiford and Lankelma[4i] discovered exceptions.

The purpose of this investigation has been to observe the effect of halogen substituted acyl groups on the molecular rearrangement of di-acyl derivatives of o-aminophenol.

The following pairs of groups were used: $—COCH_2Cl$ and $—CO_2C_2H_5$; $—COCH_2Cl$ and $—COCH_3$; $—COCCl_3$ and $—COCH_3$; $—COCCl_3$ and $—COC_6H_5$; $—CO_2CH_2CH_2Cl$ and $—CO_2C_2H_5$.

When ethyl o-hydroxycarbanilate was acylated with monochloro-acetyl chloride or when o-monochloro-acetylaminophenol was acylated with ethyl chlorocarbonate the same di-acyl was obtained. On saponification ethyl o-hydroxycarbanilate was formed which showed the compound to have been the monochloro-acetate of ethyl o-hydroxycarbanilate. In one case the monochloro-acetyl group had migrated from the nitrogen to the oxygen.

On acylating o-monochloro-acetylaminophenol with acetic anhydride a diacyl, o-monochloro-acetylaminophenyl acetate was obtained which melted at 113–114°. On reversing the order of introduction of the acyl groups a different diacyl, o-acetyl aminophenyl monochloro-acetate was obtained, melting at 128–130°. Each of these isomers on saponification

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[1] Ransom, Am. *Chem. J.*, 23, 1 (1900).

[2] Ransom and Nelson, THIS JOURNAL, 36, 390 (1914).

[3] (a) Nelson and others, *ibid.*, 48, 1677 (1926); (b) 48, 1680 (1926); (c) *Indiana Acad. Sci.*, 1921, 201–202.

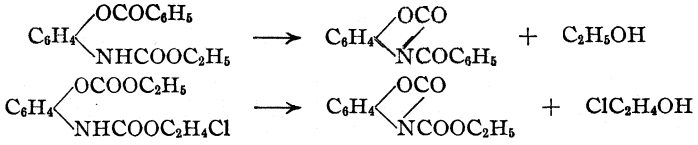
[4] (a) Raiford and others, THIS JOURNAL, 41, 2068 (1919); (b) 44, 1792 (1922); (c) 45, 469 (1923); (d) 45, 1728 (1923); (e) 46, 430 (1924); (f) 46, 2051 (1924); (g) 46, 2246 (1924); (h) 46, 2305 (1924); (i) 47, 1111 (1925); (j) 47, 1454 (1925); (k) 48, 483 (1926).

produced o-acetylaminophenol. A molecular rearrangement evidently took place during saponification. In this case the acetyl group, which is the lighter and also the less acidic, attached itself to the nitrogen atom.

When o-trichloro-acetylaminophenol was acylated with acetic anhydride a diacyl, o-trichloro-acetylaminophenyl acetate was obtained, which on saponification produced o-trichloro-acetylaminophenol. Evidently in this case the heavier and more acidic group was attached to the nitrogen. Attempts to prepare this compound or its isomer by introducing the acyls in the reverse order were unsuccessful.

o-Trichloro-acetylaminophenol was acylated with benzoyl chloride, producing the diacyl, o-benzoylaminophenyl trichloro-acetate. On saponification this produced o-benzoylaminophenol, showing that a rearrangement had taken place and that the formula of the diacyl was $Cl_3COCOC_6H_4NHCOC_6H_5$. Spiegel and Spiegel[5] prepared this diacyl and assigned to it the formula $C_6H_5OCOC_6H_4NHCOCCl_3$. In this case the lighter and also less acidic group was found on the nitrogen atom. Attempts to introduce the acyl groups in reverse order were unsuccessful. One attempt resulted in the formation of benzenylaminophenol.

Attempts were made to acylate β-chloro-ethyl-*o*-hydroxycarbanilate with ethyl chlorocarbonate, and ethyl o-hydroxycarbanilate with β-chloro-ethyl chlorocarbonate, but in both cases a decomposition occurred and carbethoxycarbonyl-o-aminophenolwas formed. This decomposition probably compares with that observed by Ransom[1] in the dry distillation of benzoyloxyphenylurethan.



Saponification of the product gave ethyl o-hydroxycarbanilate. If the above equation represents the reaction that takes place, it would appear that the heavier and more acidic group attaches itself to the nitrogen atom in each case.

Experimental

β-Chloro-ethyl-*o*-hydroxycarbanilate ($HOC_6H_4NHCO_2C_2H_4Cl$).—This compound was prepared by Groenvik's method.[6] Four and eight-tenths g. of o-aminophenol was suspended in 200 cc. of ether and 3.2 g. of β-chloro-ethyl chlorocarbonate slowly added. The mixture was filtered and the ether evaporated. After four crystallizations from benzene the white, needle-like crystals melted at 101–103°; yield, 50%.

Anal. Calcd. for $C_9H_{10}NO_3Cl$: N, 6.49. Found: 6.33.

The other monoacyls, which have been described in the literature, were prepared by the same method.

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[5] Spiegel and Spiegel, *Ber.*, 40, 1737 (1907).

[6] Groenvik, Bull. *soc. chim.*, [2] 25, 173 (1876).

Monochloro-acetate of Ethyl-o-hydroxycarbanilate ($ClCH_2OCOC_6H_4NHCO_2C_2H_5$).—A large excess (5 cc.) of monochloro-acetyl chloride was added to 2.3 g. of ethyl *o*-hydroxycarbanilate and a drop of sulfuric acid added. The mixture was warmed for twenty minutes on a water-bath and then poured into ice water. A dark oil separated. This soon solidified and was recrystallized from dilute alcohol. The crystals were cotton-like and almost white; m. p. 114–115°.

Anal. Calcd. for $C_{11}H_{12}NO_4Cl$: N, 5.44. Found: 5.40:

This diacyl was also prepared by the Schotten-Baumann method by dissolving 1.85 g. of o-monochloro-acetylaminophenol in 5.6 cc. of a 10% solution of potassium hydroxide and then adding 1 cc. of ethyl chlorocarbonate. A mixed melting point with the product formed by introducing the acyls in reverse order melted at the same temperature.

It was found necessary to add the ethyl chlorocarbonate immediately upon the solution of the monochloro-acetylaminophenol; otherwise other products precipitated.

Anal. Calcd. for $C_{11}H_{12}NO_4Cl$: N, 5.44. Found: 5.43.

On saponification ethyl o-hydroxycarbanilate was formed, proving that the $—CO_2C_2H_5$ group had been attached to the nitrogen atom.

o-Monochloro-acetylaminophenyl Acetate ($CH_3OCOC_6H_4NHCOCH_2Cl$).—This compound was prepared by the method described by Jacobs, Heidelberger and Rolf.[7] It melted at 113–114°, as stated in the literature.

On saponification o-acetylaminophenol was formed.

o-Acetylaminophenyl Monochloro-acetate ($ClCH_2OCOC_6H_4NHCOCH_3$).—A large excess of monochloro-acetyl chloride was added to 1 g. of o-acetylaminophenol. A drop of sulfuric acid was added and the mixture heated on the water-bath for twenty minutes. On pouring into cold water an oil separated and soon solidified. Recrystallization from benzene or dilute alcohol gave a white, crystalline product melting at 128–130°. It was more soluble in benzene than its isomer.

Anal. Calcd. for $C_{10}H_{10}NO_3Cl$: N, 6.16. Found: 6.27.

On saponification a white solid was obtained which after purification melted at 196–197°. A mixture with o-acetylaminophenol melted at 200°, showing them to be identical.

A mixture of this product with that produced by the saponification of the isomeric o-monochloro-acetylaminophenyl acetate melted at 196–197°, showing them to be identical.

o-Trichloro-acetylaminophenyl Acetate $(CH_3OCOC_6H_4NHCOCCl)_3$ was prepared by the method of Jacobs, Heidelberger and Rolf.[7] Five cc. of acetic anhydride and one drop of sulfuric acid were added to 2.5 g. of o-trichloro-acetylaminophenol and the mixture was warmed for ten minutes on the water-bath. On pouring into cold water an oil separated and soon solidified. Recrystallization from dilute alcohol gave a snow white product melting at 85.5°.

Anal. Calcd. for $C_{10}H_8NO_3Cl_3$: N, 4.73. Found: 4.76.

Some trouble was encountered on saponification of this compound. It was finally carried out in this way: 3 g. of o-trichloro-acetylaminophenyl acetate was dissolved in 7.8 cc. of 10% ammonium hydroxide. The solution became very dark. This was filtered and acidified. The small amount of dirty white crystals which formed was extracted with ether and the ether solution washed with a dilute solution of sodium carbonate and then with water several times. The ether was evaporated and the resulting crystals melted at 155°. A mixture of this with o-trichloro-acetylaminophenol (m. p., 160°)

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[7] Jacobs, Heidelberger and Rolf, THIS JOURNAL, 41, 458 (1919).

melted at 154–160°, showing the two to be identical. The amount of saponification product obtained did not permit recrystallization.

Attempts to prepare *o*-trichloro-acetylaminophenyl acetate or its isomer from *o*-acetylaminophenol and trichloro-acetyl chloride resulted in failure.

o-Benzoylaminophenyl Trichloro-acetate ($\mathrm{Cl_3COCOC_6H_4NHCOC_6H_5}$).—This compound was prepared by the method of Spiegel and Spiegel.[5] The crystals were white, lustrous plates melting at 104°.

On saponification o-benzoylaminophenol was formed.

Benzenylaminophenol ($\mathrm{NC_6H_4OCC_6H_5}$).—This compound was formed when an excess of trichloro-acetyl chloride was added to o-benzoylaminophenol and allowed to stand on a steam-bath for 72 hours. This was done in an attempt to prepare *o*-benzoylaminophenyl trichloro-acetate. All attempts to prepare that compound from *o*-benzoylaminophenol and trichloro-acetyl chloride were failures. The benzenylaminophenol was purified by steam distillation. The crystals were colorless needles melting at 103"; yield, 73%. They showed all the properties described by Ladenburg.[8]

Anal. Calcd. for $\mathrm{C_{13}H_9NO}$: N, 7.18. Found: 7.03.

Carbethoxycarbonyl *o*-**Aminophenol** ($\mathrm{OCOC_6H_4NCOOC_2H_5}$).—This compound was formed in an attempt to prepare ethyl carbonate of *β*-chloro-ethyl *o*-hydroxycarbanilate as follows: 4.3 g. of *β*-chloro-ethyl o-hydroxycarbanilate was dissolved in 75 cc. of water which contained 1.1 g. of potassium hydroxide, and 2.2 g. of ethyl chlorocarbonate was added dropwise. The brown oil which formed soon solidified and was recrystallized twice from strong alcohol. The crystals were colorless, mica-like plates melting at 80°.

Anal. Calcd. for $\mathrm{C_{10}H_9NO_4}$: N, 6.76. Found: 6.87.

On saponification of this product ethyl o-hydroxycarbanilate was formed as shown by mixed melting point.

Carbethoxycarbonyl o-aminophenol was also formed in the same way, when ethyl o-hydroxycarbanilate in alkaline solution was treated with *β*-chloro-ethyl chlorocarbonate. This was shown by mixed melting point and the fact that the same product was formed on saponification.

In order to confirm the identification of the above products, carbethoxycarbonyl o-aminophenol was prepared by a method similar to that used by Ransom[1] for the preparation of benzoylcarbonyl-o-aminophenol. One and five-tenths g. of carbonylaminophenol was dissolved in 75 cc. of water containing a chemically equivalent amount of potassium hydroxide. One and two-tenths g. of ethyl chlorocarbonate was slowly added with shaking. The brown oil which formed soon crystallized to lustrous, mica-like plates melting at 79.5". The melting point remained the same when mixed with the product formed from the action of ethyl chlorocarbonate on *β*-chloro-ethyl *o*-hydroxycarbanilate, showing the products to be identical.

Summary

1. In three cases out of five of the diacyl derivatives of o-aminophenol prepared, it has been found that the lighter and less acidic acyl group attached itself to the nitrogen atom, while the heavier and more acidic group, containing chlorine, attached itself to the oxygen atom. In the other two cases the heavier and more acidic group containing chlorine

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[8] Ladenburg, **Ber.,** 9, 1526 **(1876).**

attached itself to the nitrogen atom. This demonstrates that neither weight nor acidity is the determining factor.

2. Several new acyl derivatives of o-aminophenol have been prepared and studied.

WEST LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE LABORATORIES OF PHYSICAL CHEMISTRY AND AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

A QUANTITATIVE STUDY OF THE PHOTOCHEMICAL ACTIVATION OF STEROLS IN THE CURE OF RICKETS

BY RUSSELL J. FOSBINDER, PARRINGTON DANIELS AND HARRY STEENBOCK

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Recent discoveries in chemical physiology, showing that rickets can be cured by sterols which have previously been exposed to ultraviolet radiation,[1] offer interesting possibilities for photochemical investigations. The study appears attractive because the severity of rickets and its cure can be measured fairly quantitatively and because the antirachitic activation of the curative agent—the sterols—can be effected by such small amounts of energy that monochromatic light obtained with a spectrometer may be used.

In the present investigation an attempt was made to determine quantitatively the amount of energy necessary to secure a demonstrable deposition of calcium in the bones of a rachitic rat. This determination not only gives an idea of the extreme sensitiveness of the physiological reaction but, together with spectrographic evidence, indicates also that while cholesterol of even more than ordinary purity can be activated, the effect is probably due to a contaminant. This, hypothesis is in harmony with the recent suggestions of other investigators.[2]

The absorption spectrum of cholesterol was determined first because it was not available in the literature when the investigation was started. Since it could not be taken for granted that all portions of the absorption region are necessarily concerned in the activation process, cholesterol was exposed in different parts of the spectrum and tested physiologically.

Experimental Procedure

The source of light was a 220-volt quartz mercury vapor lamp loaned by the **Hanovia** Chemical and Manufacturing Company. It was operated on a 500-volt D. C. current with suitable resistances and a reactance in the circuit. After bringing the lamp to equilibrium by running it for some time, the resistances were so adjusted as to give a current of 2.4 amperes and a potential drop of 130 volts across the lamp terminals. For

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[1] (a) Steenbock, Black, Nelson, Nelson and Hoppert, *J. Biol. Chem.*, 63, xxv (1925); (b) Hess and Weinstock, ibid., 63, xxv (1925); (c) Rosenheim and Webster, Lancet, 1925, p. 1025.

[2] Rosenheim and Webster, *Biochem. J.*, 21, 389 (1927).

purposes of stability the base of the lamp was fixed in position with a plaster of Paris cast. The entire lamp was enclosed in a large ventilated box in order to prevent stray radiations.

The radiations of the lamp were resolved by means of a Hilger quartz monochromator which was provided with a helical drum graduated from 200 to 800 millimicrons. Its graduation was checked with reference to the well-known lines of the emission spectrum of sodium and the mercury arc. The collimator slit was set at a width of 0.5 or 1 mm. and the instrument gave ample separation of the different lines as proved with photographic plates.

The intensity of irradiation was measured with a Coblenz vacuum thermopile connected with a Leeds and Northrup galvanometer. The thermopile was provided with a fluorite window and the 10 silver-bismuth junctions had a total area of 13.5 square mm. It was mounted on a sliding rack behind the slit so that it could be raised to allow the radiation to strike the sample of cholesterol.

The thermopile-galvanometer system was calibrated in absolute energy unit· with a standard filament lamp (No. C44, U. S. Bureau of Standards). A radiation intensity of 5.4×10^{-7} watts per square mm., after allowing for a slight correction for the fluorite window, produced a deflection of 28 mm. on the galvanometer scale. The galvanometer had a sensitivity of 15 mm. per microvolt.

It was found necessary to adjust the spectrometer and lamp very carefully, because any shift in their relative positions which might be hardly noticeable was sufficient to reduce the intensity of the emergent light greatly. This adjustment was made by setting the spectrometer with its slit 10 cm. from the end of the lamp and then turning it until the thermopile gave a maximum deflection.

Ordinary purified cholesterol which had been shown to be activatable[1a,b,c] was used as the absorbent for the ultraviolet radiations. All of the experiments were carried out with one preparation known as V-1-24. It represented cholesterol which had been obtained as a commercial product from the Wilson Laboratories. It was purified by further saponification with alcoholic potassium hydroxide, diluted with water and extracted with ether. After evaporation of the ether the residue was crystallized repeatedly from purified ethyl alcohol. The above preparation represented the crystallizations from the alcoholic mother liquors of the 28th to the 40th fractions. It was found in the course of other experiments to be more activatable than the ordinary material.

For exposure to the monochromatic radiations the cholesterol was packed in a little rectangular box of sheet copper, held in a vertical position by a spring clamp directly behind the thermopile slit. The box was slightly larger in area than the slit and 2 mm. deep and it held approximately 50 mg. of cholesterol crystals packed tightly. The crystals were cemented together by the addition of a little ether, which evaporated rapidly. This quantity of cholesterol was vastly greater than the amount required for complete absorption of the radiations. Great care was taken that the cholesterol was exposed in the exact position previously occupied by the thermopile—a procedure which was made relatively easy by the mechanical arrangement.

The tests for activation and quantitative degree of activation were carried out with rats, using the line test as developed in the Johns Hopkins Laboratories.[3] Rickets was produced in the animals by feeding the Wisconsin 2965 ration[4] for a period of three to four weeks. When the rickets was of a severe type, as indicated by the peculiar shambling gait of the animal and the accompanying enlargements of the distal ends of the radii and ulnae, the exposed sample of cholesterol was taken up in ether and poured over 50 gm. of the ration and the ether evaporated. This material was fed to the

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[3] McCollum, Simmonds, Shipley and Park, *J. Biol. Chem.*, 51, 41 (1922).

[4] Steenbock and Black, *ibid.*, 64, 263 (1925).

animal daily with consumption control and when completely consumed was followed with the original 2965 ration until a total of ten days had elapsed. The animals were then killed with ether, the distal ends of the radii and ulnae removed, split with a scalpel and stained with a silver nitrate solution. The amount of calcium deposition was described as negative, positive or very positive.

The first attempts in this work led to failure because it was not known how long an exposure to make nor what part of the absorption spectrum is the most efficient. The pioneering work, which was done some time before any publications appeared from other laboratories, was done by spraying a solution of cholesterol in ether on a glass plate with an ordinary atomizer. There was thus deposited a uniform film of cholesterol. This film was exposed in a large quartz spectrograph with a dispersion of 25 cm. for wave lengths between 200 and 800 millimicrons. After an exposure of ten hours the plate was lowered slightly to expose fresh areas and this procedure was repeated 8 times. A sheet metal mask with long vertical slots corresponding to various sections of the mercury arc spectrum was then fitted over the plates and the cholesterol in each of these slots was scraped out and tested separately by means of the feeding technique already described. It was found in this manner that only those wave lengths shorter than 313 millimicrons were effective in the process of activation. These results corresponded exactly with what had been reported by Hess and Weinstock[5] for the upper limits of the active region when ultraviolet light cures rickets by direct action upon the animal. In all the later experiments the monochromator and thermopile were used and the results will be published later in detail. For the present research most of the experiments were carried out using the 265-mercury vapor line. This line was chosen because it possesses a sharp maximum, well separated from other radiation and also because at this time a large number of experiments had definitely established that this region was particularly effective in the photochemical reaction.

Experimental Results

The experimental results are summarized in Table I.

TABLE I

INFLUENCE OF QUANTITY OF RADIATION OF 265 $m\mu$ WAVE LENGTH ON CURATIVE EFFICIENCY

Time of irradiation, seconds	Energy absorbed, ergs	Number of quanta absorbed $\cdot nx10^{13}$	Antirachitic action
2400	24,960	350	Very positive
1200	12,480	175	Very positive
600	6,240	87.5	Very positive
300	3,120	43.7	Very positive
150	1,560	21.8	Positive
75	780	10.9	Positive
45	468	6.5	Positive
22.5	234	3.2	Positive
11	117	1.6	Negative
5	52	0.8	Negative
2.5	26	.4	Negative
1.25	13	.2	Negative

It is evident from these data that with the mercury line at 265 $m\mu$, a minimum energy input of 234 ergs is necessary to give a positive test for

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[5] Hess and Weinstock, *J. Amer.* Med. *Assoc.*, 80,687 (1923).

the deposition of calcium in a rat suffering with rickets. This energy input corresponds to an exposure of 22.5 seconds under the conditions of the experiment.

Similar experiments were carried out with three other lines and in a later research all the lines were carefully investigated. Single observations failed to give positive results with the 257 line at 350 ergs. The 280 line required 1170 ergs and the 302 line 2730 ergs.

Calculations

The following specific calculation shows how the number of quanta absorbed, as recorded in the third column of Table I can be calculated from the thermopile readings.

Galvanometer deflection on 265 mμ (g) $= 4$ mm.
Galvanometer deflection with standard lamp, $(s) = 28$ mm.
Radiation from standard lamp $= 5.4$ ergs per second per sq. mm. under conditions specified by the Bureau of Standards
Area of slit, $(a) = 13.5$ sq. mm.
Time of radiation, $(t) = 22.5$ seconds
Total radiation, (E), $= g/s\,a\,t\,(5.4$ ergs$) = 4/28 \times 13.5 \times 22.5 \times 5.4 = 234$ ergs

According to the quantum theory the total radiation (E) $= nhv$, where $n =$ the number of quanta, $h =$ Planck's constant of 6.54×10^{-27} erg seconds and $v =$ the frequency of the light. For light of 265 mμ, $v = (3 \times 10^{10}$ cm. per sec.$)/(2.65 \times 10^{-5}$ cm.$) = 1.1 \times 10^{15}$ sec.$^{-1}$. Then $n = E/h\nu = 234/(6.54 \times 10^{-27} \times 1.1 \times 10^{15}) = 3.2 \times 10^{13}$ quanta.

According to Einstein's law of photochemistry each quantum of light produces a molecule of activated material, provided that all the light is used in the photochemical reaction. According to this assumption 3.2×10^{13} molecules of vitamin D were synthesized by the 3.2×10^{13} quanta during the exposure of 22.5 seconds.

The number of gram molecules may be obtained by dividing the number of molecules by the Avogadro number, as follows: $(3.2 \times 10^{13})/(6.06 \times 10^{23}) = 5 \times 10^{-11}$ g. molecule. Assuming that the molecular weight of the antirachitic material is essentially the same as that of cholesterol (385) the number of g. of vitamin D may be calculated as follows: weight of vitamin D synthesized $= 5 \times 10^{-11} \times 385 = 2 \times 10^{-8}$ g. This calculation indicates that about twenty billionths of a gram of vitamin D is sufficient to produce calcium deposition in a rachitic rat.

Conclusions

The calculation just given indicates that a quantity of vitamin D so small as to defy any chemical test is sufficient to initiate a cure of rickets. It is difficult then to draw definite conclusions concerning the antirachitic properties of irradiated material from the gross chemical or physical properties.

The validity of the Einstein law may well be questioned **and** there are many reactions in which it does not apply. The greatest discrepancies appear in highly polar systems such as in the photochemical combination of chlorine and hydrogen, where a chain mechanism is assumed to account for the large number of molecules produced by each quantum. In the photo-activation of a sterol it is not easy to imagine a mechanism which will greatly vitiate the Einstein relation, and the assumption of the validity of the Einstein law is certainly justified as a first approximation. The calculation indicates that about 2×10^{-8} g. of vitamin D is sufficient to give a positive effect on a **100** g. rat and this quantity is smaller than the quantity of adrenaline or other drugs which can be detected by the most delicate physiological tests.

This calculation though indirect is probably more accurate than any direct measurement now available, for even the greatest refinement in the purification of cod-liver oil still leaves a great excess of inactive material. It is probable, however, that in the future, pure vitamin D can be isolated which will have the sensitivity predicted in this research. Already in a recent investigation by Rosenheim and Webster[2] it has been found that 1×10^{-7} g. of a sample of irradiated ergosterol is sufficient to give a positive test.

It must be emphasized that the calculation of 3.2×10^{13} quanta given here is based on the assumption that all the light absorbed by the purified cholesterol **(V-1-24)** was converted into vitamin D. Probably some of the light was absorbed by material which is not converted into vitamin D and further purification of the pro-vitamin in future preparations should lead to greater efficiencies. It is to be expected then that the minimum quantity of 2×10^{-8} g. calculated here may be still further reduced.

The authors wish to acknowledge the help of Mr. Kenneth G. Bulley,[6] who carried out some of the preliminary work.

Summary

1. A quantitative photochemical investigation using monochromatic light from a spectrometer has been made possible by utilizing a sensitive physiological test for the cure of rickets.

2. **3.2** $\times 10^{13}$ quanta of light of 265 mμ produced sufficient vitamin D from purified cholesterol to affect a rat suffering with rickets.

3. Assuming the Einstein photochemical relation it has been calculated that 3.2×10^{13} molecules or 2×10^{-8} g. of vitamin D is sufficient to give a detectable deposition of calcium.

4. Similar experiments with purer pro-vitamin may show that this minimum quantity may be still further reduced.

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[6] B. S. *Thesis*, University of Wisconsin, June, 1925.

NEW BOOKS

Laboratory Manual of General Inorganic Chemistry. By M. CANNON SNEED, Professor of Chemistry, University of Minnesota, and RAYMOND E. KIRK, Assistant Professor of Chemistry, University of Minnesota. Ginn and Company, 15 Ashburton Place, Boston, Massachusetts, 1927. xvii + 181 pp. 61 figs. 14 × 21.5 cm. Price $1.20.

This manual follows the order of Sneed's "General Inorganic Chemistry." More experiments are included than will normally be performed by any single class. Topics of a diversified nature have been selected to give the instructor a choice of material. Specific directions regarding the amounts of material are given wherever possible. The manual contains directions for 246 experiments divided into 44 divisions or chapters, which deal with the usual groups of the periodic table and special topics such as atomic theory, gas laws, molecular weights, calculations, solution, equilibrium and speed, ionization, periodic system, oxidation and reduction, thermo-chemistry, colloids, chemistry of living processes and many special directions for inorganic preparations. The manual contains many excellent line drawings of apparatus.

EDWARD MUELLER

Laboratory Manual of Inorganic Chemistry and Elementary Qualitative Analysis. By C. C. HEDGES, Head of Department of Chemistry and Chemical Engineering, and H. R. BRAYTON, Professor of Inorganic Chemistry in the Agricultural and Mechanical College of Texas. D. C. Heath and Company, 239 West 39th Street. New York City, 1927. 233 pp. 16.5 × 23 cm. Price $1.48.

This manual is intended for college students who receive from three to five hours weekly of laboratory instruction. It is printed on one side of gummed, perforated paper (interleaved with paraffined sheets) and parts of directions may thus be torn out to paste in the notebook in which the student records his data. For convenience the work is outlined by weeks and it is suggested that the "start-stop" method of instruction be used: when a number of experiments have been performed emphasizing a general principle the entire group is halted for a discussion; then new experiments are begun. The manual indicates considerable effort to solve the problems of "mass-education."

The manual is divided into two parts. The first deals with general principles and common materials such as oxygen, hydrogen, valence, acids, bases, salts, various non-metallic elements, ionization, some proximate tests of textiles, of vegetable oils, of soap, etc. The second part deals with the properties of metals, and qualitative analysis. The experimental work is simple; no complicated or expensive apparatus, an important factor with large classes, is required. This manual will interest particularly those teachers who are confronted with the handling of large classes in elementary chemistry.

EDWARD MUELLER

The Constitution of Glass. A series of Papers Reprinted from the Journal of the Society of Glass Technology. Edited by W. E. S. TURNER, D.Sc. The Society of Glass Technology, Darnall Road, Sheffield, England, 1927. vii + 191 pp. 62 figs. 14 × 22 cm.

As the title indicates, this is not a new work, but a reprint, including ten papers by thirteen authors. Eight of the papers, including the leading article by Professor Turner himself, formed part of a general discussion held in 1925 on the "Constitution of Glass," while two others were contributed later. They are here assembled, repaged and indexed for convenience of reference.

ROBERT B. SOSMAN

Kinetic Theory of Gases: Being a Text and Reference Book Whose Purpose Is to Combine the Classical Deductions with Recent Experimental Advances in a Convenient Form for Student and Investigator. By LEONARD B. LOEB, Associate Professor of Physics in the University of California. First edition. The McGraw-Hill Book Company, Inc., 370 Seventh Avenue, New York City, 1927. xvi + 555 pp. 76 figs. 15.5 × 23.5 cm. Price $5.50.

The author has been "much hampered by lack of a handy reference book containing a collection of the classical and more modern aspects of the kinetic theory." The book was written "in an attempt to meet this situation." The reviewer finds no reference in the acknowledgments made in the preface to J. H. Jeans' fine treatise now in its fourth edition, although in the text this most important work in the field is referred to abundantly.

The book reviews in six chapters the classical kinetic theory in elementary fashion. A chapter is devoted to the interesting investigations of Knudsen and there is also included a brief discussion of the "Brownian" movement. The chapter of the "Handbuch der Radiologie," vol. 6, written by P. Debye entitled "Theorie der electrischen und magnetischen Molekulareigenschaften" has been partially translated and makes an appropriate addition to the volume. The concluding chapter on the application of kinetic theory to the conduction of electricity in gases is in the field of the author's work and is well and interestingly written.

The important problem of the distribution of velocities in a molecular stream is touched upon by the author and some confusion may disturb the mind of the reader regarding the quantity "average velocity of the molecules in the stream." The author computes (p. 99) the root mean square value $\sqrt{\bar{c}^2} = \sqrt{4kT/m}$ but designates it the average value which can be found to be $\bar{c} = \sqrt{9/8\ \pi\ kT/m}$. The discussion of the equation of state which is of particular interest to the physical chemist is of the usual textbook variety and all reference to the work of the last fifteen years is lacking. Even the fact that the Joule experiment has been successfully performed has escaped the author's notice. In this connection also it is noted that the calculation of the cohesive pressure as a/v^2 is made to depend on an integral $2\pi/3\ n^2 \int \phi(r)\ r^3 dr = a$. This integral has passed from one book to another for a long time, although it is clear that the lower limit must be from the distance of contact of the molecules, as for example the diameter, for spheres. The treatment of the properties of real gases is on the whole perfunctory.

The treatment of the viscosity of gases is of the standard elementary type and the rather illusory "Sutherland theory" is reproduced, which is disappointing in view of the elegant treatment of the temperature dependence of gaseous viscosity given so long ago by Enskog and Chapman. Passing on to the subject of the viscosity of liquids the author states that, "Hence the viscosity in liquids is governed by cohesive forces entirely and shows little dependence on density." This is odd since the cohesive pressure is mainly a function of the volume. Moreover, Figs. 36, 37 and 38 show immediately that the viscosity is very much a function of the volume. The author has evidently overlooked entirely H. B. Phillips' interesting treatment of the viscosity of liquids now some six years old.

The most important problem of the theory of gaseous diffusion is treated in twenty pages and the Fourier series formula (p. **233)** is incorrectly given.

The review of low pressure phenomena is very welcome and the thoughtful reader will be impressed with the great amount of work both theoretical and practical which remains to be accomplished. The review of the question of so-called "Thermal Transpiration" is well done and it is hoped will be improved in a future edition because of its very fundamental connection with molecular forces.

The author has discussed the magnetic deflection of atomic streams but the treatment leaves much to be desired. It is hoped that few readers will prove as naïve as the author in supposing that a final and unambiguous decision has been reached regarding the quantization of magnetic moments which it is stated has "been definitely proved by a direct and unmistakable experiment." Certainly many serious minds will be relieved if it turns out that the "switch into position" of the elementary magnets is caused by the existence of a stray field of a few gauss in the "oven chamber." It is interesting to note in this connection that for the moment the analogous electric-field experiment shows no quantization of molecular dipoles.

It would be ungracious not to commend the final chapter on electrical conductivity of gases. The author is evidently more at home in this field and one can only regret that more space was not given to this subject where the problem fairly bristles with difficulties which should intrigue the interest of the really interested student of nature.

F. *G.* **KEYES**

Statistical Mechanics with Applications to Physics and Chemistry. By RICHARD C. TOLMAN, Ph.D., Professor of Physical Chemistry and Mathematical Physics, California Institute of Technology. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue at 29th Street, New York, 1927. **334** pp. 15.5 X **23.5** cm. Price 57.00.

The author has never demonstrated his courage more conspicuously than in the present successful attempt at a presentation of the much abused subject of Statistical Mechanics; a subject which however and by whomever belabored has never refused to yield at least what was already well known. Professor Tolman has evidently "lived with" his subject long enough to know its pitfalls, its elegancies and its possibilities. Indeed its richness in possibilities must remain, at least for a long time yet, one source of its intriguing interest. The chemist in particular must ultimately cultivate the subject seriously since, as the author points out, certain chemical phenomena are often especially susceptible to the mode of thought.

Professor Tolman's treatment of mechanics (classical) is brief but the work of the English masters in this subject is readily available and the eight pages suffice. The properties of "Statistical Ensembles" is in the opinion of the reviewer too brief, certainly, for chemists who as a class are only beginning to formulate their ideas in symbols. The Ergodic hypothesis (most readers would perhaps prefer Maxwell's term "principle of continuity of path") receives deserved and competent discussion and the author's form of statement should prove acceptable. The reviewer hopes the treatment in the next edition will be expanded.

The introduction into statistical mechanics of the so-called quantum theory (Chapter 7) gives rise to many problems, especially in the absence of any final form of the quantum theory. The difficulties, however, detract but little from the usefulness of the development since, as the author points out, Einstein's general considerations relative to absorption and emission and Bohr's energy level relations provide much of the solid material required for the extension of statistical mechanics.

The subject of gaseous specific heats is treated and for hydrogen in particular. The general subject is of the most fundamental and practical importance to chemists. Why the directly observed values of the specific heat of hydrogen at higher temperatures (1600–2000") should continue to be "explained" quantum-wise is still puzzling since too much is explained in view of the fact that a considerable fraction of hydrogen's apparent specific heat at these high temperatures is absorbed by dissociation of the molecules. The whole theory of gaseous specific heats is, however, in its infancy.

The presentation relative to the most probable state of a system is based very largely on the treatment of Ehrenfest and Trkal, the notation of which is not altogether enticing. The method of deducing the value of the special Dirichlet integral $\int \ldots \int dx_1\, dx_2\, dx_3 \ldots dx_m$ is also in-elegant. A proof of some generality, modeled for example after that in Augustus de Morgan's "Differential and Integral Calculus," p. 678, might perhaps appeal more to many readers.

The vapor pressure of crystals, glasses and gaseous equilibrium follows. The latter treatment only makes progress under the limitation of constant specific heat capacities. Many readers will undoubtedly leave the demonstration (Chapter 14) with the feeling that the difficult problem of calculating a gaseous equilibrium by statistical mechanics is far from solved.

Chapters 15, 16, 17, with those dealing with chemical reaction rate, are in the writer's best vein. The Chapter 19 as relates to transport problems could well have been omitted. The reference to Knudsen as the discoverer of the relation $p_2/p_1 = \sqrt{T_2}/\sqrt{T_1}$ is an error (section 251, page 207), as a reference to Maxwell's papers, Vol. 2, p. 708, will show. The discussion of reaction rate theory is frankly from the particular point of view of the author, which requires no apology.

The volume is an important and welcome addition to the American Chemical Society Series of Scientific Monographs.

F. G. KEYES

Tabellen zur allgemeinen und speziellen Mineralogie. (Tables for General and Special Mineralogy.) By DR. PAUL NIGGLI, Professor of Mineralogy at the University of Zürich. Gebrüder Borntraeger, Berlin, Germany, 1927. xvi + 300 pp. 228 figs. 17 X 25 cm. Price, bound, 9.3 M. ($2.25).

Niggli's comprehensive three-volume "Textbook of Mineralogy"[1] is too expensive to be owned by every worker in the subject, much as he would like to have it always at hand; while the Departmental Library's copy of so useful a work is always likely to be in the temporary possession of some borrower. Hence these tables, condensing and making readily accessible the principal facts and classifications of the larger work, have been issued at a price within the reach of all. There are seven tables (25 pp.) in general crystallography, followed by 161 pages of determinative tables, based primarily upon crystallographic criteria and secondarily upon habit and luster. This is the core of the book. Next follow classifications of the common minerals, based upon color and hardness, streak, density, forms of growth, and manner of occurrence (28 pp.). Tables of the uses of minerals (25 pp.) make an interesting digression. A well-illustrated grouping of the rock-forming minerals according to optical properties and certain other features observable under the microscope (52 pp.) completes the book. If one were assembling a half-meter shelf of books to stand beside the petrographic microscope, this book should certainly be among them

ROBERT B. SOSMAN

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[1] For reviews of Vols. 1 and 2 see *Nature.* 119, 595 (1927); THIS JOURNAL, 49, 1389 (1927). Vol. 3 is in preparation.

Annual Survey of American Chemistry. Vol. II. July 1, 1926 to July 1, 1927. Edited by CLARENCE J. WEST, Director, Research Information Service, National Research Council. Under the auspices of the Division of Chemistry and Chemical Technology, National Research Council, William J. Hale, Chairman. The Chemical Catalog Company, Inc., 419 Fourth Avenue, New York, 1927. 415 pp. 13.5 × 21.5 cm. Price $3.00.

In the preparation of the first volume of the "Annual Survey of American Chemistry" the unique plan was adopted of dividing the science into a large number of topics of limited scope and having experts, active in research, report on the work in their particular fields. The plan led to well balanced, authoritative reviews and proved to be more satisfactory than the procedure adopted in similar publications in which the authors covered a wide range of subjects often far from their own intimate experience. The second volume of the survey is a marked improvement over the first as the result of the extension of the subjects treated. Physical chemistry is now covered more adequately. The present volume contains chapters on theories of solution, gases and gas mixtures, phase rule equilibrium data, thermodynamics, colloids, catalysis, photochemistry, crystal structure and x-rays. The recent advances in inorganic and organic chemistry both pure and applied are well covered. Fifty-one of the leading research workers in the country have contributed to the volume. An author index adds to the value of the book. As a similar index was not prepared for the first volume it is included here.

The book will be of great value to everyone interested in the growth of chemical knowledge. In these days of extreme specialization and high pressure activity no one can find time to read adequately and broadly. It is a privilege to have an expert tell us what has been done in his own particular field.

The only adverse criticism the reviewer has heard of the annual surveys is that they cover American research only; chemistry knows no national boundaries; why should the scope be limited? Very practical reasons, which must be self-evident to any one, led to the restriction imposed. It is to be earnestly hoped that the success of the present venture will lead to an annual survey of world chemistry prepared as the result of international cooperation, and following the plan of having limited fields reviewed by a large number of active investigators.

An examination of the book will give the reader a large amount of information of value, because American chemists are taking a leading place in research. He will learn what our universities and great industrial research organizations are producing—what his friends, acquaintances and men whose names are known to him are doing in chemistry. The study of the survey by graduate students is much to be desired. Their interest in chemistry will be developed. Their desire to attend scientific meetings will be aroused if they know who are the active workers and what they are doing. In short they will be inspired to read more and do more; and every good teacher preparing men for a life work in chemistry has this ideal continuously before him. "The Annual Survey of American Chemistry" will help.

JAMES F. NORRIS

Anleitung für das organisch-chemische **Praktikum.** (Laboratory Manual of Organic Chemistry.) Third, revised edition. By Dr. FRANZ WILH. HENLE, former lecturer at the University of Strassburg. Preface by Prof. Dr. J. Thiele. Adakemische Verlagsgesellschaft m.b.H., Leipzig, Germany, 1927. xii + 308 pp. 55 figs. 14.5 × 22.5 cm. Price, unbound, 12 M; bound, 14 M.

Mistakes which appeared in the second edition have been eliminated in this new edition. Additional sketches of apparatus, directions for ten new preparations and rewritten directions for a number of others have been included. Numerous new literature references appearing since 1920 have been added to the various experiments.

Most instructors who have had other than very beginning classes in organic laboratory are familiar with one of the earlier editions of this book. In case there are those who do not know it, it may be stated that the manual includes ninety preparations of widely varying type. A large number of references are given after each preparation, which have to do not alone with the individual preparation involved but with its homologs and with its more important reactions with which a student should be familiar. It is noticeable that the author has, for the most part, limited his references to the German literature, though in many instances pertinent investigations have appeared in the foreign literature.

Anyone who has occasion to teach organic chemistry laboratory classes should have this volume at hand.

ROGER ADAMS

The Methods of Organic Chemistry, a Laboratory Manual. By C. W. PORTER, T. D. STEWART and G. E. K. BRANCH, Members of the Faculty of the College of Chemistry in the University of California. Ginn and Company, 15 Ashburton Place, Boston, Massachusetts, 1927. vi + 311 pp. 35 figs 14.5 X 21.5 cm. Price $2.00.

The appearance of a new laboratory manual in organic chemistry is of such common occurrence that a reviewer is inclined to read it rather critically to determine what it may contain that is novel. This book, designed either for a one or two semester course, is divided into five parts—(I), Mechanical Operations; (II), Organic Preparations; (111), Class Reactions—a System of Qualitative Analysis; (IV), Acids, Bases and Indicators; (V), Quantitative Analysis.

Part I, which covers distillation, extraction, filtration, etc., describes not only how the operations are carried out, but at the same time it is written in such a way as to impress the reader with the fundamental principle involved in each operation. Great care has been taken to go into such detail that a perfectly clear understanding of what is meant by vapor pressure, boiling point, fractional distillation, etc., is made possible. This chapter appeals to the reviewer as superior to others which are found in manuals of this sort.

Part II on Organic Preparations does not appear to have anything characteristic about it. The preparations are, of course, selected to cover a wide range of type reactions. Two experiments might be mentioned which are not found in one or another of the laboratory manuals now available—the preparation, illustrating a Grignard reaction, of diphenylcarbinol from benzophenone and ethylmagnesium bromide, and the preparation of tetraphenylpinacol by the action of ultraviolet light on an alcohol solution of benzophenone. Each of the approximately fifty experiments is followed by questions pertinent to the preparation involved.

Part III on Qualitative Analysis consists of over 100 pages and is designed, as is stated by the authors, for the primary purpose not of identification of individual compounds, but for the determination of characteristic groups or radicals and the development of a thorough understanding of class reactions. The usual manual attempts to give only a very little space, or none at all, to this important part of organic chemistry. In this chapter the discussion of the various reactions as to general applicability and limitations is excellent. From the experimental standpoint the value of the chapter is doubtful. After a student is familiar with the material presented it is questionable whether, if given an unknown, he would be in a position to identify the class of substances to which it belongs. Certainly he would have to use an undue amount of time or to have a large amount of help from the teacher.

A few points of interest in connection with the material in this chapter might be mentioned. For determining the Du Claux constants on volatile acids, previous writers have always advised phosphoric or sulfuric acids. These authors use nitric acid. It is surprising that this acid does not occasionally lead to difficulties on account of the low boiling point, 120°, of the constant boiling mixture with water. The authors have used hydroxylamine for identifying aldehydes and ketones; it has been found in the laboratory of the reviewer that in general phenylhydrazine is easier to use and more often gives good results. Nitrous acid has been selected for distinguishing primary, secondary and tertiary amines, whereas in the reviewer's experience benzene sulfonyl chloride has been found in general to be more suitable for this use. Frequently the tests are based on titrations and other quantitative methods, when in many instances the same information could be obtained by simple qualitative tests. Naturally, a procedure developed along the quantitative line will require much more time to produce the same results.

Part IV, a valuable addition to the book, discusses in detail acids, bases and indicators, and brings out as is done in no other elementary organic manual the important facts and principles involved.

Part V on Quantitative Analysis is comparatively brief and no attempt is made to go into great detail about the various procedures.

ROGER ADAMS

Lehrbuch der Cellulosechemie. (Textbook **of** Cellulose Chemistry.) By DR.-ING. **EMIL HEUSER,** Hon. Professor at the Technical High School of Berlin. Third Edition. Gebriider Borntraeger, Schoneberger Ufer 12a, Berlin W. 35, Germany, **1927.** xi + 278 pp. **3** figs. 16 X 24.5 cm. Price 16.80 M.

The appearance of a third edition within seven years is some index of the popularity and general excellence of Dr. Heuser's textbook on cellulose chemistry. The author maintains his previous position in dealing with cellulose as a chemical individual, in stressing the fundamentals and in relegating empiricism and technology to a subordinate place. Again (in this edition) we find chapters on alcoholate formation, on cellulose esters and ethers, on the oxidation and degradation of cellulose and on the constitution of cellulose—but all of these chapters (with the exception of the introduction) have been rewritten and enlarged and are replete with references to the newer literature which covers most of the advances in the cellulose field through August, 1927. One brief but very timely chapter on the investigation of cellulose by means of x-rays has been added. It is little more than a synopsis but gives a valuable bibliography and is written by Professor R. O. Herzog, eminent director of the Kaiser Wilhelm Institut für Faserstoffchemie at Berlin-Dahlem.

Dr. Heuser is to be congratulated on the thoroughness with which he has reviewed most of the literature and on the terseness with which his material is presented. Especially interesting are the chapters on alcoholate formation and on the cellulose esters wherein the author's own researches on the mercerization and viscose reactions are clearly described. The chapter on the constitution of cellulose is, however, a bit disappointing. Apart from the error in reproducing Hibbert's formula on p. 245 (an obvious misprint), it appears to the reviewer that the author has not maintained quite the proper balance and sense of proportion in dealing with constitutional formulas for cellulose. A number of the older formulations (like those of Tollens and Green) hardly merit the amount of space allotted to them. They are historically important and interesting, but (as Dr. Heuser himself shows) they are not in harmony with the more recent experimental data. On the other hand, constitutional formulas such as those proposed by Schorger and by Gray deserve at least a fleeting mention. However, these are minor defects in an excellent, clearly-written book which in its third edition cannot fail to aid and stimulate research workers and technologists interested in the chemistry of cellulose.

LOUIS E. WISE

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF PRINCETON UNIVERSITY]

I. THE EFFECT OF RADIATION ON THE DECOMPOSITION OF OZONE AND NITROUS OXIDE

BY JAMES H. HIBBEN[1]

RECEIVED AUGUST 18, 1927 PUBLISHED APRIL 5, 1928

The radiation hypothesis has been subjected to many proposed theoretical modifications. Experimentally there has been little direct substantiation of either the simple hypothesis or the more complex substitutes. The failure of absorption bands to correspond with the activating frequency, as calculated from the critical increment, has been noted.[2] Most significant have been the observations of H. A. Taylor[3] and Daniels[4] that the decomposition of nitrogen pentoxide is unaltered by infra-red radiation. This has been extended by the latter to include the oxidation of alcohol vapor and the decomposition of hydrogen chloride. Regardless of the particular mechanism of molecular activation by radiation, there should be a disturbance in the reaction rate when the available energy from the possible activating frequencies or frequency is increased. The present work provides two more examples of chemical gas reactions which are unaffected by infra-red radiation.

Experimental Part

Gaseous nitrous oxide and ozone were both exposed to the infra-red radiation emitted by a carbon arc. The latter consumed 20 amperes and was located 10 cm. from the reaction vessels. A 200cc. transparent quartz tube and a similar glass tube with sealed on polished fluorite window, served as reaction vessels. Thermal conduction from the arc was avoided by means of air currents and filters. Except from the side exposed to the arc, the vessels were surrounded by an electric furnace or ice-bath and kept at constant temperature.

It is obvious that the radiation density of any possibly activating

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[1] National Research Fellow.

[2] Langmuir, THIS JOURNAL, 42, 2190 (1920), and others.

[3] H. A. Taylor, *ibid.*, 48, 577 (1926).

[4] Daniels, *ibid.*, 48, 607 (1926).

frequencies in the infra-red must be materially increased in order that there may be any material alteration in the reaction rate. The actual radiation density at different frequencies from a carbon arc (at 3800° K.) is calculable from Planck's radiation law. However, only a part of the emitted radiation actually falls on the reaction vessel. Of this part a portion is reflected and a portion adsorbed, the amount depending on the frequency. The actual radiation received by the gas in the vessel is only a small part of the emitted energy. The foregoing considerations lead to the following conclusions for these particular experiments: namely, (1) that for wave lengths longer than 2.5μ there is no appreciable increase in their radiation density within the reaction vessel, as a result of exposure to the arc, the reaction vessel being at 883° K.; (2) that for wave lengths longer than 9.6μ there is likewise no appreciable radiation density increase resulting from the arc's emission, the reaction vessel being at a temperature of 273° K. The possible effectiveness of the infra-red radiation, therefore, is experimentally limited to these spectral regions; that is, in the case of nitrous oxide decomposition to 2.5μ and in the case of the ozone decomposition to 9.6μ.

The decomposition of the nitrous oxide was followed by means of a mercury manometer connected to the apparatus with a capillary tube and the increase in pressure during the reaction measured. The reaction was repeated several times at the same initial pressure. With complete illumination, with total darkness and with alternate illumination and darkness there was *no alteration in the reaction rate.* The temperature was maintained at 883° K. by means of an electric furnace. At lower temperatures, with the fluorite window vessel, no effect was noticeable. While the velocity constant at half-time decomposition is in agreement with the value found by Hinshelwood and Burk,[5] the total variation of the constant is over twofold greater than that observed by them. The values are as follows.

TABLE I

DECOMPOSITION OF NITROUS OXIDE

Total press., mm. of Hg	Partial press., N_2O	Time, minutes	$K \times 10^6$, seconds
227	227	0	..
237	207	200	7.1
250	181	400	9.3
262.5	156	600	11.1
272.5	126	800	12
287.5	106	1000	16.3
300	81	1200	20
312.5	56	1400	28.4
320	41	1600	37.2

The values are the same whether the nitrous oxide be illuminated or the reaction carried out in the dark. The nitrous oxide was obtained from

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[5] Hinshelwood and Burk, *Proc. Roy. Soc. (London),* 106A, 284 (1924).

cylinders but was distilled and dried before using. The departure from the homogeneous bimolecular reaction rate was attributed (by Hinshelwood) to the effect of by-products in reaction. The time of half decomposition at different initial pressures indicates, nevertheless, a bimolecular reaction.

Similar experiments were carried out with ozone. The ozone was prepared by means of a discharge in oxygen at 0.1 mm. pressure, the discharge tube being immersed in liquid **air.** When several cubic centimeters of the liquid ozone had collected, the oxygen was pumped off and the ozone allowed to distil into the previously evacuated reaction system.

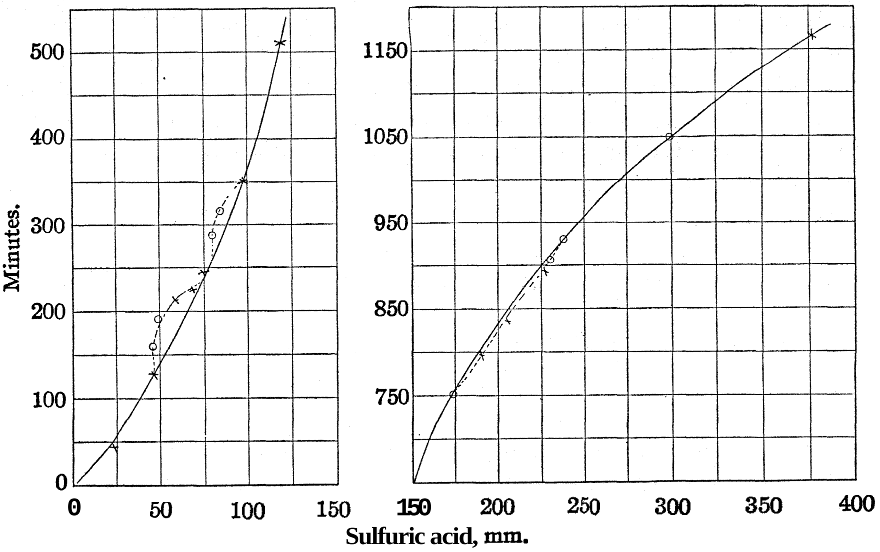

Fig. 1.—Ozone decomposition.

The product varied from 60 to 75% pure ozone after distillation. The reaction vessel was immersed in an ice-bath. The surface exposed to the arc lamp was unprotected, however, except by means of an air stream. The reaction vessel was connected to a sulfuric acid manometer by capillary tubing and the reaction was followed from the increase in pressure. A certain amount of segregation of different portions of the infra-red spectrum was possible by the use of quartz, biotite and iodine in carbon disulfide filters. The visible and ultraviolet were eliminated in each experiment. There was no appreciable alteration in the decomposition rate on alternate illumination and darkening. A typical curve is presented in Fig. 1. The light reaction is represented by X and the dark by O. The curve is divided into two parts, the first being from 0 to 550 minutes and the second from 650 to 1200 minutes. An appreciable expansion is noticeable on illumination. An equivalent contraction, however, takes place when the light is cut off. Due to the erratic behavior of ozone decompositions, the alternate dark and light reactions were necessarily tried within the same experiment. An inter-experiment comparison as in the case of nitrous oxide decomposition is not practical.

Summary

A simple, homogeneous, high temperature reaction, the decomposition of nitrous oxide, has been investigated from the point of view of the radiation hypothesis and found unresponsive to an increase in the radiation density of frequencies corresponding to the infra-red.

A heterogeneous low temperature reaction, the decomposition of ozone, has similarly been found to be uninfluenced by infra-red radiation.

In view of the somewhat similar experiments with nitrogen pentoxide, hydrogen chloride and alcohol,[3,4] together with the failure of predicted activating frequencies to correspond with absorption bands,[2,3] molecular activation through the absorption of single or multiple frequencies seems improbable.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF PRINCETON UNIVERSITY]

II. THE LOW PRESSURE DECOMPOSITION OF NITRIC AND NITROUS OXIDES

BY JAMES H. HIBBEN[1]

RECEIVED AUGUST 18, 1927 PUBLISHED APRIL 5, 1928

In a previous publication[2] the various radiation and collision theories of molecular activation were mentioned, together with some experimental data. Of the most significance to the present publication, which deals with collisions in chemical gas reactions, however, is the original theory of Lindemann.[3] This has been amplified by Hinshelwood[4] and others.[5] Lindemann has accounted for the existence of unimolecular reactions by the assumption that dissociation does not take place instantly on collision but only after a time which, on the average, is greater than that necessary to reestablish Maxwellian distribution. Otherwise the rate of dissociation would depend on the rate by which this distribution was reestablished or upon the collision frequency. At high pressures, the concentration of active molecules is therefore maintained constant and the

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[1] National Research Fellow.

[2] Hibben, *Proc. Am. Acad. Sci.*, **August,** *1927.*

[3] Lindemann, *Trans. Faraday Soc.*, 17, 598 *(1922).*

[4] Hinshelwood, *Proc. Roy. Soc. (London),* **113A, 230** *(1926).*

[5] (a) Fowler and Rideal, *ibid.*, **113A,** 570 *(1926);* (b) Rice and Ramsperger, THIS JOURNAL, 49, *1617 (1927);* *(c)* Lewis and Smith, *ibid.*, 47, *1514 (1925).* Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, 13, *188 (1927).*

reaction unimolecular. But at low pressures, when the time between collisions is of the same order as the average life of a molecule after attaining its critical velocity, the apparent unimolecular reaction will become dependent on collision frequency, or bimolecular. Experimental verification of this phenomenon has been obtained by Hinshelwood,[6] who has noted that the decomposition of propionic aldehyde changes from unimolecular toward a bimolecular reaction at a pressure of approximately 80 mm. of Hg, and the decomposition of diethyl ether similarly changes at 150 mm. of Hg. To the contrary, however, Hirst and Rideal[7] have noted that in the decomposition of nitrogen pentoxide, instead of changing from unimolecular to bimolecular at very low pressures, the reaction actually increased in velocity until the decomposition followed the Rideal-Dushman equation. The decomposition at high pressures[8] follows the equation

$$-\mathrm{d}c/\mathrm{d}t = 4.98 \times 10^{13}\, e^{-24{,}700/RT}C$$

while at low pressures this becomes, according to Rideal

$$-\mathrm{d}c/\mathrm{d}t = 2.39 \times 10^{14}\, e^{-24{,}700/RT}C$$

corresponding to the Rideal-Dushman equation

$$-\mathrm{d}c/\mathrm{d}t = v\, e^{-Nhv/RT}C$$

Lindemann's theory presupposes that for a unimolecular reaction the rate of activation must exceed the rate of decomposition. For simple bimolecular reactions the rate of reaction may be expressed as a function of the collision freyuency of activated molecules.[9] The number of molecules reacting per cc. per second is

$$[\text{Equation 1}]\ N = 2\sqrt{2}\,\pi\,\sigma^2\bar{u}\,n^2\,e^{-Q/RT}$$

where a is the molecular diameter, $\bar{u}$ the root mean square velocity, n the number of molecules per cc. and $e^{-Q/RT}$ the fraction of the total number activated. In the case of apparently unimolecular reactions, however, it seems that the decomposition rate is in excess of the activation rate thus calculated, which is incompatible with Lindemann's theory. To account for this divergence[10] Hinshelwood makes the assumption that the total energy E could be made up by any distribution among a considerable number of degrees of freedom instead of two as generally used. This leads to the following expression.

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[6] Hinshelwood, *Proc. Roy. Soc. (London)*, **113A,** 221 (1926); *ibid.,* **114A,** 84 (1927).

[7] Hirst and Rideal, *ibid.,* **109A,** 526 (1925).

[8] Daniels and Johnston, THIS JOURNAL, 43, **53** (1921).

[9] (a) *W. C.* McC. Lewis, *J. Chem. Soc.,* 113,471 (1918); (b) Hinshelwood and Burk, *Proc. Roy. Soc. (London),* **106A,** 284 (1924).

[10] See references 3 and 4. It might be mentioned that here the postulates of Fowler and Rideal, of Rice and Ramsperger, and of Hinshelwood differ from one another chiefly in approximations and simplifications.

$$\text{[Equation 2] } N = \frac{Z\, e^{\left(\frac{-Q + (1/2n' - 1)RT}{RT}\right)} \left[\left(\frac{Q + (1/2n' - 1)RT}{RT}\right)^{1/2n' - 1}\right]}{1/2n' - 1}$$

where N is the number of molecules which react per second per cc., Z the total number of collisions calculated from the equation $Z = 2\sqrt{2}\,\pi\,\sigma^2\bar{u}\,n^2$ and n' is the number of degrees of freedom. The number of degrees necessary to satisfy the experimental conditions for propionic aldehyde decomposition is 12 to 14, and for diethyl ether 8 degrees of freedom. The equation may be applied only when the pressure is known where the assumption can be made that there are just enough collisions to account for the number of molecules which react, that is, at the beginning of the transitions between unimolecular and bimolecular reaction.

In view, therefore, of the fundamental theoretical importance attached to the behavior of unimolecular reactions at low pressures not only from the point of view of Lindemann's theory but also from that of any proposed chain, quantum chain, or ternary collision hypotheses,[11] it seemed pertinent to attempt to provide some experimental data on the behavior of chemical gas reactions at low pressures. For this purpose a unimolecular and a simple homogeneous bimolecular reaction were chosen.

As has been mentioned, Hirst and Rideal studied the decomposition of nitrogen pentoxide down to a total pressure of 4.5×10^{-2} mm. of mercury. Their results were not in accordance with Lindemann's theory. The reaction velocity increased with decreasing total pressure, the transition beginning at approximately 0.25 mm. of mercury. As their results showed considerable inter-experimental variation, it seemed justifiable to repeat this work. The bimolecular reaction selected was the decomposition of nitrous oxide. The results obtained in both cases were somewhat unexpected.

Experimental Part

1. Nitrous Oxide

Apparatus.—The reaction system used for the study of the decomposition of nitrous oxide is pictured in Fig. 1. It consists essentially of a quartz reaction vessel of about 200cc. capacity, a pressure manometer and a pumping system. The latter included one rotary oil pump, one two-stage mercury vapor pump and one Deauvillier type mercury vapor pump. The reaction vessel was connected to the condensation trap, the pumping system and manometer by means of a graded seal. The reaction was followed in two ways (A) by condensing out everything except the products of the reaction, nitrogen and oxygen, and measuring their pressure at definite time intervals, (B) by measuring the total pressure of the system and calculating the decomposition from the increase in pressure. The two methods gave concordant results.

Of the greatest importance was the pressure measuring device. This was a Pirani-

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[11] (a) Christiansen and Kramers, *Z. physik. Chem.*, 104, 451 (1923); (b) Langmuir, THIS JOURNAL, 42, 2201 (1920); (c) Tolman, *ibid.*, 47, 1524 (1925); (d) Born and Franck, Z. *Physik*, 31, 411 (1925).

Hale manometer with some modifications. As the temperature in the quartz bulb was considerably above that of the gage the volume of the latter could not exceed a few cubic centimeters. The platinum wire, as in the usual design, was strung vertically up and down in the same manner as the vacuum electric light bulbs. However, the distance from the wire to the sides of the gage was only a few millimeters. This results in increased sensitivity per unit volume. The gage can now function as a resistance thermometer, so is extremely sensitive to fluctuations in the temperature of the walls. It was found necessary to place the gage in the interior of a large aluminum block, both gage and block being immersed in an accurately controlled thermostat. The heat capacity of the block compensates for fluctuations in the temperature of the circulating water of the thermostat. The second departure from the usual design of a Pirani gage was in the size of the platinum wire used. This was about 50 cm. of 0.1 mm. pure platinum wire, or three times the diameter generally employed. It must be wound tight enough so that there is no give, but not so tight that there is a strain on the wire. An important feature in the preparation of this manometer is the fact that the wire is heated at atmospheric pressure to a dull red for several hours before using. This con-

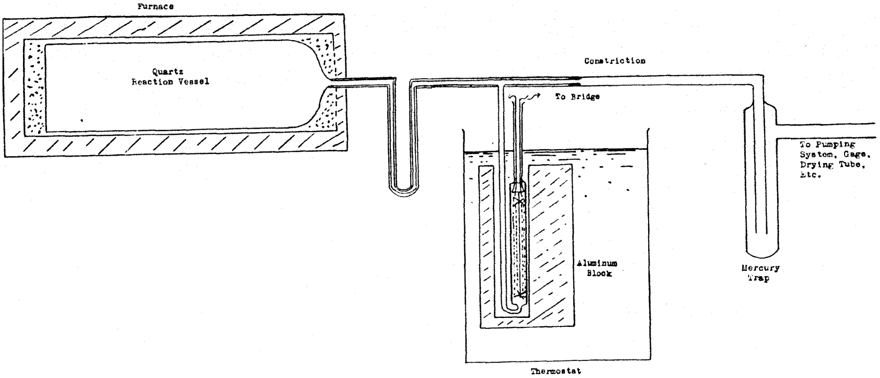

Fig. 1.—Apparatus for nitrous oxide decomposition.

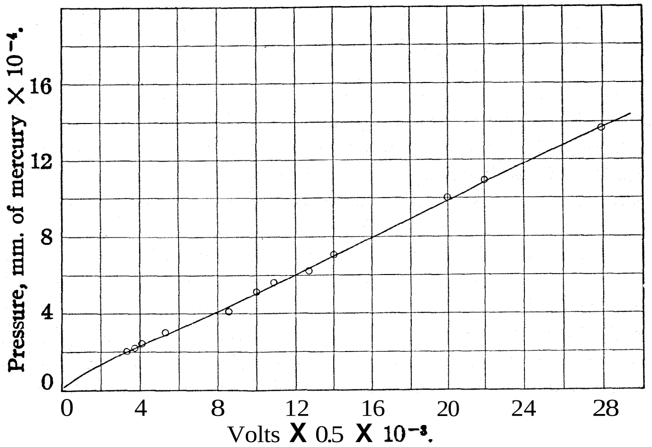

Fig. 2.—Calibration curve for Pirani type gage.

verts the wire to a stable, crystalline structure of constant resistance. With these precautions the manometer will give constant readings for months at a time, in spite of repeated baking and repeated changes in pressure from a vacuum to one atmosphere. The wire was maintained at constant temperature by means of a Callender and Griffiths bridge and the electromotive force input into the bridge measured with a potentiometer. This is Campbell's method.[12] The usual exponential formula $(V^2 - V_0^2)/V_0^2$ (where V is the electromotive force at pressure read and V_0 electromotive force at best vacuum) was not necessary, as the direct electromotive force calibration against pressure was practically a linear function. Sample calibration curves are given in Figs. 2 and 3. The platinum wire was kept at 17.76° above the bath temperature, 30.1°.

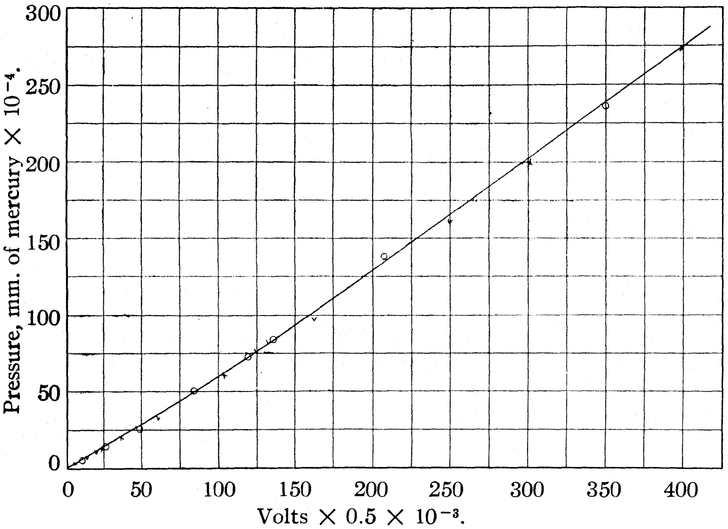

Fig. 3.—Calibration curve for Pirani type gage.

Procedure.—The general procedure in an experiment was to bake out the entire reaction system at 300°, allow the requisite amount of previously purified nitrous oxide to enter, seal off the pumping system and then follow the reaction by pressure measurements. Inasmuch as the reaction is bimolecular, the first experiments were carried out at a very elevated temperature to obtain any clecomposition in a reasonable time at low pressures. This, incidentally, led to the observation that above 1000" K. the quartz vessel may be permeable to carbon dioxide and water vapor. No amount of superheating or pumping would reduce the enormous quantities of these gases admitted. It was observed, however, that the decomposition at these temperatures was instantaneous. At 600° K. the quantity of carbon dioxide was nrgligible and the pressure of the water vapor kept at 10^{-3} mm. of mercury by means of a carbon dioxide-ether trap constantly present.

Results.—The results are given in Table I (see Fig. 4).

Interpretation of Results.—The reaction velocity is approximately 1000 times faster than the calculated value for the bimolecular decomposition of nitrous oxide at these temperatures and pressures, using the equation of Hinshelwood and Burk.[9b] The velocity constants calcu-

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[12] Campbell, *Proc. Phys. Soc.*, **33**, 257 (1921).

TABLE I

THE DECOMPOSITION OF NITROUS OXIDE

Partial pressure of N_2O, 1/100 mm. Hg	Time, minutes	K, unimolecular constant
Curve 1. 625° K.		
2.68	...	....
1.85	6.5	0.023
1.36	30	.021
.80	78	.0155 (total pressure method)
.60	90	.0166
.26	170	.0138
Curve 2. 550° K.		
3.17		....
1.81	16.8	.033
1.71	28.0	.022 (total pressure method)
1.31	64.0	.0137
.51	172.0	.011
Curve 3. 605° K.		
7.53	...	....
6.20	23.4	.0161 (condensation method)
2.60	66.6	.0159
.53	132.0	.019

lated as a unimolecular reaction are in fair agreement, particularly in the latter half of each reaction. The initial part of the reaction is somewhat complicated by the adsorption of appreciable quantities of the gas. The

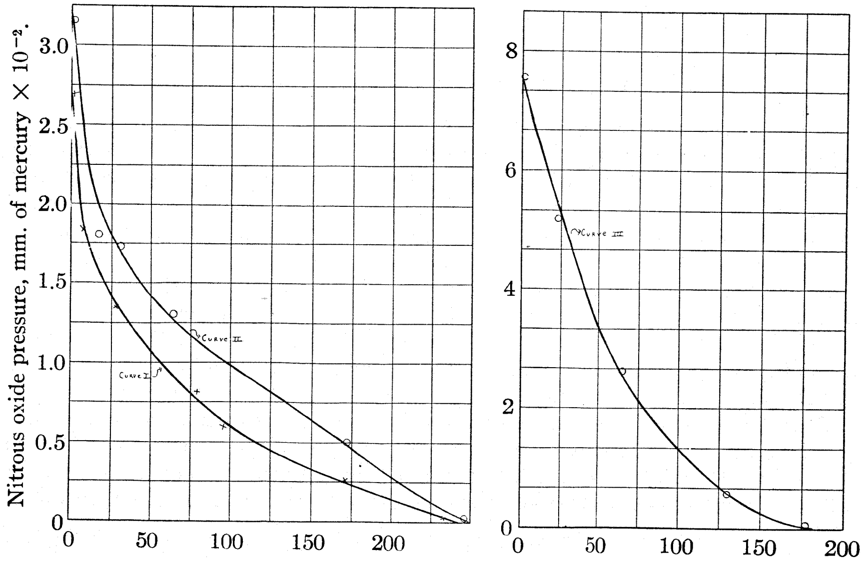

Fig. 4.—Nitrous oxide decomposition.

most logical explanation of this phenomenon seems to be that the reaction at low pressures is entirely heterogeneous.

2. Nitrogen Pentoxide

Nitrogen pentoxide was selected as the unimolecular reaction to be investigated at low absolute pressures, partially because of the effect observed by Hirst and Rideal, as mentioned, and partially because the reaction has been found to remain truly unimolecular throughout a series of rigid experimental investigations.[7,13]

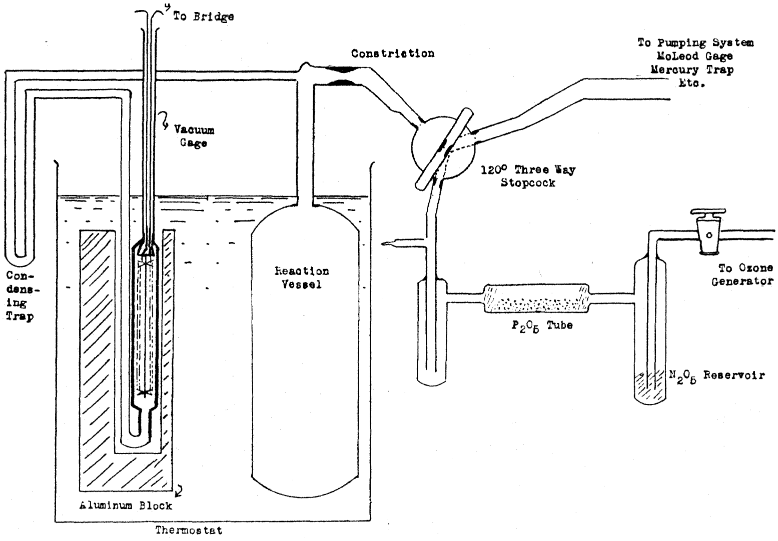

Fig. 5.—Apparatus for nitrogen pentoxide decomposition.

The experimental arrangement for this investigation was substantially that developed to study the nitrous oxide decomposition. The reaction vessel in this case, however, was immersed in the same thermostat as the vacuum gage. The latter, as before, was inside an aluminum block but was connected across to a one and one-half liter bulb by means of a short piece of tubing containing a small condensation trap outside the thermostat. A "T" insertion in this same tubing led to the same evacuating system previously used. This was constricted for sealing off after the pentoxide admission. A three way 120° stopcock permitted an interchangeable connection between the pumping system and reaction system, between the former and the pentoxide reservoir, and between the reservoir and the reaction system. Thii is illustrated in Fig. 5.

Procedure.—The thermostatic system was so designed, after the manner of Hirst and Rideal, that it could be removed and the entire reaction system baked out at 300°. The nitrogen pentoxide in the reservoir at −78° had previously been prepared from nitric acid and phosphorus pentoxide and purified by repeated distillations in ozone at −10°. As many as ten distillations were necessary to remove all visible traces of ni-

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[13] (a) Daniels, Wulf and Karrer, THIS JOURNAL, 44, 2402 (1922); (b) White and Tolman, *ibid.*, **47**, 1240 (1925); (c) Hunt and Daniels, *ibid.*, **47**, 1602 (1925); (d) Busse and Daniels, *ibid.*, **49**, 1257 (1927).

trogen dioxide. This product was then distilled into the nitrogen pentoxide reservoir of the experimental system proper, where it could be washed with an ozone stream before using. It was then evacuated and distilled in *vacuo* from the reservoir into the first trap and then the surplus distilled back again and kept in liquid air. The reservoir-trap stopcock was then closed and the pentoxide allowed to distil from the first trap into the reaction system, where it was condensed with liquid air in the condensing trap just outside the thermostat. Pressure measurements at this point indicated an entirely negligible decomposition on admission. Pressure measurement of the total pressure at the end of the reaction as compared with the calculated total pressure from the pentoxide decomposition indicated possibly a trace of nitrogen dioxide originally present or decomposed stopcock grease vapor. The pressure of the pentoxide is practically identical with the total pressure of the system.

After the pentoxide was entirely condensed, the pumping system was connected to the reaction system and the constriction sealed off with pumping. The pentoxide was then reevaporated. At intervals it was condensed and the residual oxygen pressure measured. The nitrogen pentoxide decomposed is twice the oxygen pressure. The experiments were carried out in the dark.

Results.—The results are as shown in Table II.

TABLE II

DECOMPOSITION OF NITROGEN PENTOXIDE

Time, minutes	Decomposed $N_2O_5 \times 10^{-2}$ mm. of Hg	K, unimolecular vel. const.
Experiment I. **30.1°**		
32	2.54	0.0047
110	7.0	.0042
170	9.4	.0042
275	12.8	.00422
442	15.8	.00427
∞	18.6	
Experiment **II. 30.1°**		
18	1.0	0.005
44	2.32	.005
88	4.20	.0051
139	5.6	.0048
259	8.0	.0046
499	10.3	.0045
∞	11.5	
Experiment **III. 30.1°**		
20	1.2	0.0056
17	2.1	.0056
67	3.3	.0052
130	5.4	.00506
277	8.2	.00476
412	9.6	.0048
877	11.0	.0046
∞	11.2	

Time, minutes	Decomposed $N_2O_5 \times 10^{-2}$ mm. of Hg	K, unimolecular vel. const.
Experiment **IV. 30.1°**		
11	0.18	0.00562
58	.82	.0054
94	1.12	.00496
196	1.84	.00486
311	2.30	.00468
471	2.64	.0045
931	2.95	.0044
∞	2.955	
Experiment **V. 40.0°**		
18	2.5	0.0168
60	6.0	.0166
105	7.8	.0165
139	8.5	.0162
259	9.35	.0160
∞	9.5	
Experiment **VI. 30.1°**		
147	0.16	0.010
∞	.18	...
Experiment **VII. 30.1°**		
45	1.20	0.00473
135	2.84	.00450
205	3.81	.00451
335	4.84	.00450
w	6.20	

The initial pressures utilized in the study of the nitrogen pentoxide decomposition were (in 10^{-4} mm. of mercury) 18, 295, 620, 950, 1120, 1150 and 1860.

Discussion of Results

The final velocity constant values are probably nearest to the correct value since traces of any foreign matter such as stopcock grease vapor and mercury oxide would tend to make the initial decomposition greater. This is borne out by Experiment VII in which excessive precautions were taken to keep the grease vapor at a minimum and by Experiment I. In the latter, the initial decomposition due to such vapor would be less noticeable because of the greater total initial pressure. Furthermore, a similar increase of the same magnitude in the case of the nitrous oxide decomposition indicates that a small variation in the constant is possibly inherent in low pressure systems due to initial adsorption on the glass walls. In the sixth experiment the larger value found for the constant is without great significance, as the error in the oxygen pressure measurement and the effect of foreign matter is comparatively large at this pressure. *The essential fact is that the velocity constant shows no variation in excess of the experimental errors.* This is further substantiated by the following comparison. Taking 25,000 as the critical increment, this gives at 30.1° $K = 0.0044$, found; $K = 0.00424$, calcd., the second value being calculated from Daniels and Johnston's data.

Taking, furthermore, the velocity constant values of $K = 0.0044$ at 30.1° and $K = 0.0162$ at 40°, as found, and calculating the critical increment from the temperature coefficient, the following result is obtained: critical increment, calcd., 24,775; critical increment, Daniels and Johnston, 24,700. This is better agreement than the experimental error justifies.

Outside of three qualitative preliminary experiments and one final confirmatory experiment (Experiment VII), Experiments I–VI, inclusive, represent all those carried to completion. The three preliminary ones demonstrated the presence of nitrogen dioxide initially in the system to the extent of one to two hundredths of a millimeter unless extreme precaution was taken to have as pure nitrogen pentoxide as possible in the reservoir, to wash this with ozone and finally to distil at −10° before using. Excessive precautions were taken in Experiment VII to reduce the possible influence of grease and other vapors by means of a baking out at higher temperatures and the use of traps between the last stopcock and the reaction system. As a result there is a small reduction in the total variation of the velocity constant.

Notwithstanding, therefore, a hundred-fold variation in pressure, from 0.18 to 18×10^{-4} mm. of mercury, the reaction velocity of the nitrogen pentoxide decomposition remains substantially constant and in excellent agreement with the values found by Daniels and Johnston at much higher pressures.

As has been previously mentioned, Hirst and Rideal studied the decomposition of nitrogen pentoxide between total pressures in the system of 0.045 to 1.45 mm. of mercury. Beginning with a total pressure of 0.25 mm., their velocity constant increased as the total pressure decreased until a limiting value of five times the original was approximately reached at a few hundredths of a millimeter total pressure. The reaction velocity then followed the Rideal-Dushman equation. This was explained by the assumption that one-fifth of the molecules undergo decomposition irrespective of pressure, but that four-fifths undergo decomposition only if they do not suffer collisions with other molecules for a period of 10^{-6} seconds after activation. This permits the energy in one oscillator to pass to another in the same molecule, a process requiring something of the order of 10^{-6} seconds.

It is immediately apparent that the results obtained by the writer are not in agreement with those of Hirst and Rideal. Certainly no alteration in the velocity constant of the same order of magnitude as observed by them was present. From an examination of their data it may be briefly pointed out here that the change in the velocity constant during an experiment as noted by them, due to the pressure change in the course of the reaction, is not in agreement with a corresponding velocity constant change due to different initial pressures in different experiments as it should be. Furthermore, the actual pentoxide present in the beginning of their reactions was generally only 50% and occasionally only 25% of the total pressure. This was due to decomposition on admission and no doubt was a complicating factor.

It is also apparent that no evidence of initial transition between unimolecular and bimolecular reaction is present. At 0.01 mm. pressure about 10^{-10} more molecules react than is explainable from the simple collision theory (Equation 1). It is interesting to note that the modified form (Equation 2) will not account for this discrepancy even with the assumption of 30 or more degrees[4,14] of freedom and a transition point at 0.01 mm., which is not the case.

It might also be mentioned that the average time interval between collisions of activated molecules at these pressures is about 10^{-5} seconds. In view of the fact that the average life of an activated molecule is of the order of 10^{-6} seconds, some deactivation by radiation might be expected.

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[14] Fowler and Rideal calculate by means of their special equation sufficient energy to account for the reaction at the lowest total pressure measured by Rideal hut questionably enough for the total pressures herein obtained. Since this article was submitted for publication A. C. Ramsperger, Proc. *Nat. Acad. Sci.*, 13, 849 (1927), has found that azoisopropane decomposition shows no evidence of a transition point at pressures down to 0.025 cm. of mercury.

Rideal[7] has already pointed out that a modification of reaction velocity should take place at these low pressures if simple collision, quantum chain or chain theories of molecular activation are applicable to the decomposition of nitrogen pentoxide.

The author takes this opportunity to express his appreciation of the assistance given by Professor Hugh S. Taylor.

Summary

The decomposition of nitrous oxide has been studied at low pressure. The reaction changes from bimolecular to unimolecular. The most probable explanation seems to be that the reaction is entirely heterogeneous when the pressure is at a few hundredths of a millimeter.

The decomposition of nitrogen pentoxide was studied between the total pressure limits of 0.18 and 0.0018 mm. of mercury. The velocity constant remained essentially constant throughout this hundred-fold variation of initial pressure and was in excellent agreement with the values found by Daniels and Johnston at high pressures. This was in contradiction of the observations of Hirst and Rideal.

No evidence of a transition from a unimolecular to a bimolecular reaction as predicted from Lindemann's theory was present. Not even the assumption of 30 degrees of freedom in the nitrogen pentoxide molecules would account for the rate of activation found at low pressures.

An undisturbed life for active molecules of approximately 10^{-5} seconds seems to be without effect.

WASHINGTON, D. C.

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

OBSERVATIONS ON THE RARE EARTHS. XXVII. I. FRACTIONAL PRECIPITATION OF THE CERIUM GROUP EARTHS BY ELECTROLYSIS. II. SOLUBILITY OF RARE EARTH OXALATES IN NITRIC ACID[1]

BY J. W. NECKERS WITH H. C. KREMERS

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I. Fractional Precipitation of the Cerium Group Earths by Electrolysis

Electrolysis of neutral salt solutions of the rare earths will cause the formation of hydroxide at the cathode. Due to difference in basicities of the rare earth elements, a fractionation may be effected in this manner. Dennis and his co-workers[2] electrolyzed solutions of the rare earths using

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[1] Part of a thesis submitted by J. W. Neckers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

[2] Dennis and others, THIS JOURNAL, 37, 131 (1915); 37, 1963 (1915); 40, 174 (1918).

a platinum anode and a mercury cathode. They effected separations of lanthanum from praseodymium and erbium from yttrium. Both nitrate and chloride solutions were used.

Brinton[3] has recently determined the P_{H} values of several of the rare earth solutions at the point at which the hydroxide began to precipitate. The values of **6.83,** 7.00, 7.05 and **8.35** are given for samarium, neodymium, praseodymium and lanthanum hydroxides, respectively. A confirmation of Brinton's values is shown in the electrolytic fractionation here described. Approximately 8% solutions were used.

A potential of 6 to 7 volts was found to give the best results.

The anode was made of platinum and was isolated by means of a porous porcelain cup.

A mercury cathode was always employed. Glass containers were used for cells. The electrolyte was stirred during electrolysis. The hydroxide fractions formed in most cases filtered fairly well although at times their gelatinous nature caused trouble. The following series of fractionations are reported.

Series I

Fifteen liters of 8% solution of lanthanum and praseodymium chlorides were used. Tabulated results are given in Table I.

TABLE I

LANTHANUM-PRASEODYMIUM

No.	Time, hrs.	Voltage, v.	Current, amp.	Wt. of oxide, g.	Color of oxide	Remarks
1	7	6	3.5	..	....	Manganese impurity
2	5	6	3.0	25	Chocolate brown	High % of Pr
3	1.5	5.8	4.8	17	Chocolate brown	High % of Pr
4	1.3	6.2	5.0	15	Chocolate brown	High % of Pr
5	1.5	6	3.8	18	Chocolate brown	High % of Pr
6	3	6.2	1.4	14	Medium brown	50% Pr 50% La
7	4	6.0	1.2	17	Light brown	20% Pr 80% La
8	6	6.2	1.4	22	Buff brown	5% Pr 95% La
9	6	6.5	1.0	18	Light buff	3% Pr 97% La
10	5	7.0	0.9	14	Light buff	1% Pr 99% La
11	5	6.2	.9	10	Light buff	1% Pr 99% La
12	4.5	7.2	1.1	15	Light buff	1% Pr 99% La
		Residue		457	Light buff	99% La

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[3] Brinton, J. Chem. *Soc.*, 127, 2110 (1925).

Series II

The process was next applied to a mixture of all of the metals of the cerium group with a very small percentage of the yttrium group metals also present. An approximately 8% solution of 11.5 liters' volume was used under the same conditions as in Series I. A tabulation of the data follows.

TABLE II

CERIUM GROUP

No.	Time, hrs.	Voltage, v.	Current, amp.	Wt. of oxide, g.	Color of oxide	Remarks
1	7.5	6.8	0.9	14	Medium brown	Nd, Yt group, Sa, 5% Pr
2	23	7.0	1.3	49	Medium brown	Nd, Yt group, Sa, 5% Pr
3	10	7.0	3.0	41	Dark brown	50% Nd, 40% Pr, 10% Sa
4	9	7.0	3.3	23	Chocolate brown	50% Nd, 45% Pr, 5% Sa
5	14	7.0	2.7	36	Chocolate brown	50% Nd, 50% Pr
6	18	6.3	2.2	32	Chocolate brown	50% Nd, 50% Pr
7	17	6.5	2.3	36	Chocolate brown	50% Nd, 50% Pr
8	22	6.4	2.1	26	Chocolate brown	50% Nd, 50% Pr
9	18	7.0	2.3	27	Chocolate brown	50% Nd, 50% Pr
10	23	6.9	1.9	22	Chocolate brown	50% Nd, 50% Pr
11	24	7.4	1.7	29	Medium brown	35% Nd, 35% Pr, 30% La
12	27	7.0	1.7	30	Light brown	50% La, 25% Pr, 25% Nd
13	36	7 0	0.9	22	Buff	80% La, 10% Pr, 10% Nd
14	39	7.0	1.0	20	Buff	90% La, 5% Pr, 5% Nd
15	40	7.0	1.0	21	Light buff	98% La, 1% Pr, 1% Nd
16	39	7.0	1.1	15	Light buff	99% La, 1% Pr
17	35	7.2	1.2	12	Light buff	99% La, 1% Pr
18	40	7.0	1.1	11	White	100% La
19	36	7.2	1.1	10	White	100% La
20	59	7.0	1.1	12	White	100% La

Although samarium and the yttrium group metals concentrate in the first fractions, it appears possible to obtain only an efficient concentration of lanthanum.

Series III

This series was similar in composition to Series II except that the conductivity was increased threefold by the addition of 5% sodium chloride. The speed of electrolysis was thus increased correspondingly with no decrease in efficiency of separation.

Series IV

To apply this method to a more difficult separation, 12.5 liters of an 8% solution of praseodymium and neodymium chlorides (with 5% of sodium chloride) was electrolyzed. No appreciable separation or concentration occurred although several small fractions were precipitated at both ends of the series.

Discussion of Results

It appears possible to separate rare earths by electrolysis of neutral solutions only when the P_H values are separated by more than 0.25. The values given by Brinton[3] are thus substantiated.

It is possible that a more efficient separation might be obtained by using more dilute solutions and much smaller amperages. Under such conditions the method would become less practicable.

II. Solubilities of Rare Earth Oxalates in Nitric Acid

Sarver and Brinton[4] have recently determined the solubilities of several rare earth oxalates in nitric, hydrochloric and sulfuric acids at 25°.

Since there is considerable difference in solubility of the oxalates at room and at elevated temperatures, it seemed desirable to have solubility data taken at more elevated temperatures. Such data might be of value in a further study of methods of fractionation. Solubilities were accordingly run in mixtures of nitric and oxalic acids.

The solubility tests were carried out in 500cc. Florence flasks with long necks and covered with close fitting heavy watch glasses. A temperature of 90 ± 2° was maintained by means of a slightly modified steam-bath. Temperatures of 25° were maintained by ordinary methods. Excess oxalate was added to 150 cc. of the nitric acid contained in the flasks as described. Thirty-six hours with frequent shaking was considered long enough to establish equilibrium. For analysis, two 50cc. quantities of the solutions were withdrawn with a pipet, to the tip of which an efficient filter was attached, evaporated to dryness and ignited in porcelain.

TABLE III

SOLUBILITY OF OXALATES AT 90°

Grams of oxide from 100 cc. of solution

Normality of nitric acid	Oxalic acid, %	La	Pr	Nd	Sm	Dy	Yt
0.779	...	0.4421	0.3871	....	....		
1.25	...	....	....	0.8707	....		....
1.558	...	1.2377	1.0764	....	....		....
2.337	...	....	1.8467	....	....	....	....
2.50	...	....	....	1.9571	1.8779	1.8458	1.3180
3.75	...	4.6670	....	....	....		....
5.00	...	10.4160	6.8825	6.7788	5.6750	4.8470	3.0135
0.779	5	0.0302	0.0275	....	....	....	....
1.25	5	....	....	0.0915	....		....
1.558	5	0.3083	0.1639	....	....		....
2.337	5	.7517	.6932	....	....	....	....
2.50	5	....	....	0.6760	0.5457	0.4215	0.4315
3.75	5	3.5260	....	....	....	....	....
5.00	5	9.3907	5.2339	5.1263	4.1520	3.4135	1.4515

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[4] Sarver and Brinton, THIS JOURNAL, 49,943 (1927).

The solubility determinations made at 25° were in practical agreement with those published by Sarver and Brinton and hence need not be given here. The determinations made at 90° in nitric acid of various strengths and also in the presence of oxalic acid are given in Table III.

Discussion of Results

The determination of solubilities in 1.25 N acid was discontinued after it was found that the solubility was so small that no practical use could be made of such data. At 90°, especially in the 5 N acid solutions, it was found that the solution reached no definite saturation point. The solubility of the oxalate seemed to be proportional to the length of time that the excess solid salt was in contact with the solution. This was shown by the fact that neodymium oxalate in contact with the 5 N acid for a few hours yielded 5.7060 g. of oxide from 100 cc. of the solution while if it stood for three days the oxide weighed 8.8596 g. This is probably due to the formation of oxalonitrates and the data under the hot, concentrated acid may well be called a comparison of the rate of decomposition rather than of the solubility. (The solubility, however, is a function of the rate of decomposition.) Therefore, to obtain data which would, in a graphic form, show a comparison of the solubilities, the different oxalates were submitted simultaneously to the same solubility treatment, under like conditions for the same length of time. The data resulting from the procedure are those used in the 5 N, 90° series.

It is observed that the solubilities of the oxalates at 90° is of the same order as at 25°. From these data it may also be gathered that the separation of lanthanum from praseodymium is feasible by fractionation of the oxalates. Very little separation of the other members of the cerium group might be expected. Both of these facts have been proved by actual trial in this Laboratory. The separation of yttrium from holmium might also be feasible by this method.

Summary

1. It has been found possible to separate lanthanum from praseodymium and the other cerium group earths by fractional electrolytic precipitation. Addition of 5% of sodium chloride increases the conductivity, and thus the rate of precipitation, threefold without impairing the efficiency of the fractionation. Other separations in the cerium group are not feasible by this method.

2. The solubility of the oxalates of lanthanum, praseodymium, neodymium, samarium, dysprosium and yttrium has been determined in 1.25, 2.50 and 5.00 N nitric acid at 90°. A corresponding series of determinations has also been made with 5% oxalic acid added to the nitric acid.

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

OBSERVATIONS ON THE RARE EARTHS. XXVIII. THE SEPARATION OF CERIUM

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The separation methods applied to cerium are quite different from those usually applied to the rare earths. Cerium when oxidized to the quadrivalent state assumes properties sufficiently different from the other trivalent earths to effect a quantitative separation.

The oldest method using this property is that of Mosander[2] who used chlorine or bromine to oxidize the cerium. Other methods are the neutral permanganate process proposed by Stapff[3] and perfected by Roberts,[4] and the neutral potassium bromate method proposed by James.[5] From the standpoint of the preparation of cerium free from other earths or the complete removal of cerium from the other earths, the first method is inefficient due to the necessity of several successive treatment. with chlorine, making the process slow. The neutral permanganate method is rapid but does not yield pure cerium. The cerium dioxide precipitates along with the manganese dioxide, giving a very bulky precipitate which carries down with it considerable quantities of other rare earths. The potassium bromate method yields pure cerium but is very slow and expensive; long-continued boiling and excess of reagent are necessary.

One method of oxidation reported to be quite rapid is electrolytic oxidation. Knorre[6] reported the oxidation of cerous sulfate by ammonium persulfate with the precipitation of a basic sulfate. Consequently, oxidation of cerous sulfate anodically might lead to the precipitation of ceric cerium due to the formation of persulfate around the anode. Bricout[7] also reports the precipitation of ceric dichromate by the electrolysis of a slightly acid solution of cerous chromate. These two reports and others give a possibility of a cerium separation by anodic oxidation.

Experimental

(1) **Anodic** Oxidation,—Solutions of cerium earths containing 30% of cerous cerium were electrolyzed using graphite electrodes. Electrolysis of the nitrates, chlorides and sulfates of the above solutions in

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[1] This paper represents part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Mosander, *Ann.*, 48, 210 (1843).

[3] Stapff, *J. prakt. Chem.*, [1] 79, 258 (1860).

[4] Roberts, *Am. J. Sci.*, [5] 31, 350 (1911).

[5] James, THIS JOURNAL, 33, 1326 (1911); 34, 757 (1912).

[6] Knorre, *Z. angew. Chem.*, 10, 717 (1897).

[7] Bricout, *Compt. rend.*, 118, 146 (1894).

the presence of a slight excess of the corresponding acids gave deep red colorations, indicating oxidation of cerium but no precipitation. Prolonged boiling during electrolysis failed to hydrolyze the ceric cerium.

(2) Precipitation of Ceric Phosphate.—It is evident from the above results that ceric cerium can only be removed from an acid solution by the addition of an ion which will form an insoluble ceric salt. Cerium, in its tetravalent state, is very similar to zirconium and hafnium; in fact, it so characteristically resembles Sub-Group **A** of Group Four in the periodic table that cerium occupied the position now held by hafnium until the discovery of the latter. The phosphates of these quadrivalent metals are very insoluble. The addition of orthophosphoric acid or any of its salts causes immediate precipitation of ceric phosphate. The other rare earth phosphates are soluble in dilute mineral acids. Knorre[6] and others have reported ceric phosphates for the purpose of analysis.

Ignited cerium group oxides were dissolved in concentrated nitric acid and diluted to make a 10% solution. Ignition of the oxides caused 90% of the cerium to be oxidized to the ceric state.. This solution was heated to 80° and sodium phosphate solution slowly added. All of the ceric cerium was precipitated as phosphate in a heavy, flocculent form which settled well. The presence of 5% of free nitric acid prevented the precipitation of any of the other earths.

This ceric phosphate filtered well and could be washed free from the other earths. The filtrate was further treated with excess sodium phosphate and potassium permanganate slowly added. The cerous cerium still present was thus completely oxidized and removed as phosphate. Analysis of the filtrate showed the presence of less than 0.02% of cerium. The presence of this small amount of cerium is due to the slight solubility of the phosphate in nitric acid.

A 5% nitrate solution of the cerium group earths was then prepared having present 5% of free nitric acid and a slight excess of sodium phosphate. This solution was electrolyzed as described above. Ceric phosphate was thrown down as anodic oxidation took place. After prolonged electrolysis it was found that approximately 1% of cerous cerium remained in solution. This was evidently due to cathodic reduction. In another trial the cathode was surrounded by a porous cup. In a short time the cathode became coated with a gelatinous precipitate of ceric phosphate and electrolysis ceased. This method was then abandoned.

Ceric phosphate is a heavy, cream colored precipitate when thrown down from a hot solution with constant stirring. It is sparingly soluble in 5 N nitric acid. Very little solubility is indicated in nitric acid of less than 2.5 N. Ceric phosphate is very quickly decomposed with strong sodium hydroxide solution giving insoluble ceric hydroxide. This hydroxide filters well, can readily be dissolved in nitric acid and cerous oxalate precipitated from this solution by the addition of oxalic acid. A suspension of ceric phosphate in mineral acids may also be reduced to cerous phosphate by oxalic acid.

The above method was next tried on a large-scale laboratory or semi-commercial basis. Some two hundred kilos of commercial cerium group earths were treated in the following manner. The hydroxides were ignited in order to convert as much as possible of the cerium into the ceric state. A 10% nitrate solution of these oxides in the presence of 5% of free nitric acid was treated in 60-liter evaporation dishes. Phosphate precipitation was carried out at a temperature of SO°, aided by mechanical stirring. Permanganate was then added until oxidation and precipitation of ceric phosphate were complete. The cerium free earths were precipitated from the hot filtrate as oxalates, utilizing the 5% of nitric acid present as optimum condition for oxalate precipitation. The ceric phosphate after thorough washing was treated with 50% caustic soda solution in an iron vessel. The ceric hydroxide was washed free from sodium phosphates, dissolved in nitric acid and the oxalate precipitated out.

It seemed possible that this phosphate method might also be used to separate the cerium and thorium together from cerium group earths. Monazite sand was accordingly "cracked" with concentrated sulfuric acid, the excess acid fumed off and the thorium and cerium earth sulfates were dissolved in water. The solution after acidifying with a little sulfuric acid was treated with potassium permanganate. Both thorium and ceric phosphates were precipitated together. The phosphate ion of the original monazite is thus utilized. To gain complete precipitation it was necessary to add a little more sodium phosphate.

Thus it is possible, where it is not of special interest to remove thorium separately, to obtain directly from monazite sand rare earths which have been freed of thorium and cerium by one precipitation.

(3) Discussion of Results

Anodic oxidation of cerium in sulfate and nitrate solutions goes to about 90% completion with no precipitation. Addition of an ion, such as the phosphate, allows 99% oxidation and precipitation of the cerium. If other oxidation methods are used, such as the addition of potassium permanganate, the cerium is entirely removed. The obvious reason for this complete separation is the immediate removal of the ceric cerium as an insoluble substance as soon as it reaches the ceric state. There is undoubtedly an equilibrium between the cerous and ceric states during an oxidation process. In other methods used this equilibrium is shifted mostly by excess reagents or heating, both of which require considerable time as well as reagents. In this method, however, such means are not necessary, for the presence of the phosphate causes immediate precipitation of ceric cerium as fast as it is formed. In this way the equilibrium is shifted practically completely toward the ceric ion, which is forthwith precipitated, giving complete separation.

The precipitation and removal of cerium in the form of ceric phosphate, as described in this research, has several practical points worthy of consideration. In both the chlorine and potassium bromate methods at least two treatments are necessary for the complete removal of cerium, especially in large quantities. The neutral permanganate method is slow, bulky and gives a precipitate which is difficult to filter and causes much occlusion of the filtrate. Several days are required for complete reaction and a large quantity of potassium permanganate is necessary. In both the bromate and permanganate methods the excess acid which is present after dissolving the rare earths must be neutralized with calcium carbonate before the oxidation can be applied. For precipitation of the filtrate as oxalate, acid must again be added.

The phosphate method described gives 100% removal of cerium in one precipitation and is rapid. It takes a minimum of expensive oxidizing agents and the same acid concentration employed in the removal of cerium is that required for the precipitation of remaining earths as oxalates, saving time for neutralization as well as reagents. The use of the permanganate in acid solution also increases the efficiency. The neutral permanganate is only three-fifths as efficient as that used in the acid phosphate method. Also, in the acid solution, manganese dioxide is not formed in quantities to prove troublesome as in the neutral method.

It is undoubtedly possible to use other oxidizing agents for oxidizing the cerium to the tetravalent form for precipitation. It is also possible to remove thorium, zirconium and cerium completely, in one step, in the purification of rare earth ores. This should eliminate considerable time, as well as loss of rare earths and reagents, and prove a very efficient method.

Summary

Ninety per cent. oxidation may be accomplished anodically when applied to cerous sulfate or nitrate. Ceric chloride tends to decompose to cerous chloride and chlorine, so anodic oxidation is inefficient in this case. Separation of cerium is best accomplished by precipitation of a ceric compound. Addition of a soluble phosphate to a slightly acid solution of ceric nitrate causes the complete precipitation of the cerium as ceric phosphate. The other rare earth phosphates are soluble in the dilute acid. Thorium phosphate is also precipitated. Thus rare earths may be obtained free from cerium and thorium in one precipitation.

URBANA, ILLINOIS

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

OBSERVATIONS ON THE RARE EARTHS. XXIX. THE PREPARATION AND PROPERTIES OF SOME ANHYDROUS RARE EARTH CHLORIDES

BY J. H. KLEINHEKSEL[1] WITH H. C. KREMERS

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I. Introduction

Very little work has been done recently to determine the properties of the anhydrous chlorides of some of the rare earths. The literature reports several such determinations, many of which vary considerably. As early as 1853 Marignac,[2] working with didymium, prepared the anhydrous chloride but did not determine its properties. In 1905, Matignon[3] published a rather complete work on the dehydration of the chlorides of neodymium, praseodymium, lanthanum, samarium and yttrium, and determined such properties as melting point, density and heat of solution. In 1910, Bourion[4] completed his work on the dehydration of some rare earth chlorides, having used sulfur monochloride to convert the oxides to the anhydrous chlorides. More recently Baxter and Chapin[5] with several other workers have made a rather extensive study of methods of obtaining the anhydrous rare earth chlorides.

Since very pure salts of most of the rare earth metals were available in this Laboratory, it was the purpose of this investigation further to study the preparation of the anhydrous chlorides of the rare earths **and** to determine several physical properties.

II. Rare Earths Used

With the exception of thulium all of the rare earths studied were available in a high state of purity. Several of these salts were formerly prepared in this Laboratory for atomic weight work, as described elsewhere in THIS JOURNAL.[6]

The lanthanum, cerium, praseodymium, samarium and yttrium salts were entirely free from other earths. The dysprosium material con-

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[1] An abstract of a thesis submitted by J. H. Kleinheksel in partial fulfilment of the requirements of the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Marignac, *Ann. chim. phys.*, [III] 38, 148 (1853).

[3] Matignon, *Compt. rend.*, 140, 1340 (1905).

[4] Bourion, *Ann. chim. phys.*, 21, 49 (1910).

[5] (a) Baxter and Chapin, THIS JOURNAL, 33, 1 (1911); (b) 37, 526 (1915); (c) 43, 1086 (1921); (d) 44, 307 (1922).

[6] (a) Kremers and Balke, THIS JOURNAL, 40, 593 (1918); (b) Kremers and Hopkins, *ibid.*, 41, 718 (1919); (c) Owens, Balke and Kremers, *ibid.*, 42, 518 (1920); (d) Driggs with Hopkins, *ibid.*, 47, 363 (1924).

tained only small traces of terbium. This material was the same as that supplied to the Bureau of Standards for their arc spectrum work.[7]

The holmium salt was part of Fraction 22 prepared and used by Driggs and Hopkins in the determination of the atomic weight of holmium. The thulium salt, by spectrum analysis, indicated the presence of small traces of erbium and presumably also contained very small quantities of ytterbium and lutecium.

III. Dehydration of Rare Earth Chlorides

Dehydration of the chlorides was carried out in the presence of dry hydrogen chloride both at ordinary and reduced pressures.

The method used at ordinary pressures was essentially the same as that employed in other researches in this Laboratory for atomic weight work.[6]

The 25cc. quartz reaction flask shown in Fig. 1 was a modification of those used in the above-mentioned researches on atomic weights of the rare earths. The extra vertical quartz tube with side arm D was provided to accommodate the platinum-platinum rhodium thermocouple E. A wax seal-in at E was used. The melting points of the rare earth chlorides, described later, were determined in this flask. The flask was heated by a carefully controlled electric furnace. Complete dehydration of the hydrated chloride was carried out in this flask with the thermocouple in position as shown. Dry hydrogen chloride was passed into the flask through side arm A and the exit gases passed out through outlets C and D. At the completion of dehydration the salt was fused and the melting point taken by the ordinary time-temperature cooling curve method.

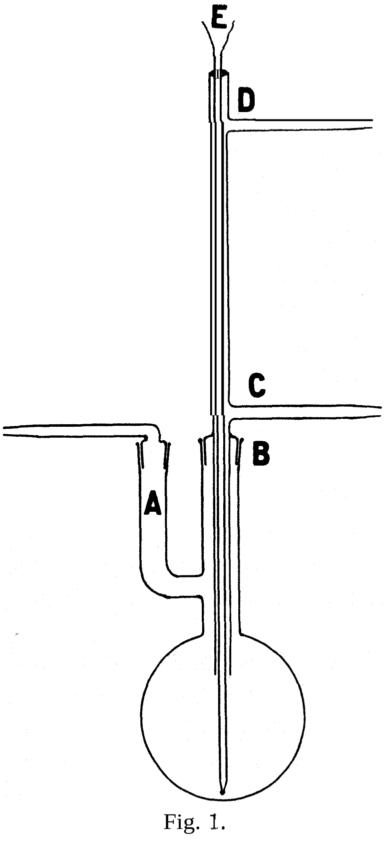

Fig. 1.

Since the first five molecules of water of hydration are removed at temperatures from 85 to 120°, depending upon the rare earth in question, there is considerable tendency for the salt to fuse during the early stages of dehydration if the temperature is allowed to rise too fast. This usually results in the formation of basic salt. Thus with the necessity of keeping the temperature well below 100° during the removal of the first five molecules of water of hydration, dehydration is very slow and usually several days were spent in carrying out one complete dehydration. Dehydration at reduced pressures overcame this difficulty completely.

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[7] *Scientific Papers,* No. **421,** Oct. 14, **1921.**

Dehydration at Reduced Pressures

Dehydration of the hexahydrated rare earth chlorides at reduced pressures was carried out in a horizontal tube furnace shown in Fig. **3.** The chlorides were placed in the quartz boats **A** contained in a Pyrex tube B with ground glass joint at D. Pure, dry hydrochloric acid gas first passed through a pressure reduction device illustrated in Fig. *2.* Inside of a glass tube A was a smaller tube B, closed at the top with a stopcock through which varying amounts of mercury were admitted, depending upon the reduction in pressure necessary. The bottom end of tube B terminated in a small, round ball of glass. This was ground in to fit perfectly on the upper end of tube C, thus acting as a valve. When the pressure in A was sufficiently reduced, tube B was raised and gas allowed to enter at E. During operation the exit D of the furnace was attached to a water suction pump. Exit D of the pressure regulator was attached to B of the furnace. Dry hydrogen chloride from the generator was allowed to enter E of the pressure regulator.

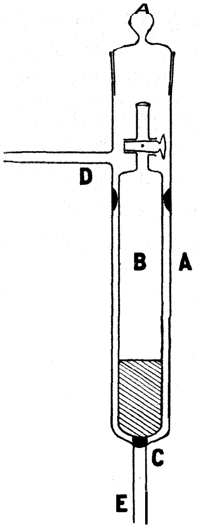

Fig. **2.**

With this reduced pressure dehydration apparatus the complete dehydration of all or any of the hydrated chlorides was accomplished within twelve hours. **A** gas flow through the tube at the rate of about one cc. per second at a pressure of about **25** cm. of **mercury** was maintained. For the first three or four hours the temperature was maintained at 70°, then was gradually raised to 160° to remove the last molecule of water, held at that temperature for one or two hours and then raised slowly to 250°. At this point all of the water of hvdration was removed. While still hot the furnace was opened, the boats quickly removed to a desiccator over sulfuric acid and allowed to cool. The samples were then transferred to hot, dry glass tubes and quickly sealed. This method gave a perfectly anhydrous product. These samples of anhydrous rare earth chlorides were used in the density and heat of solution determinations as well as those samples obtained from the melting point determinations.

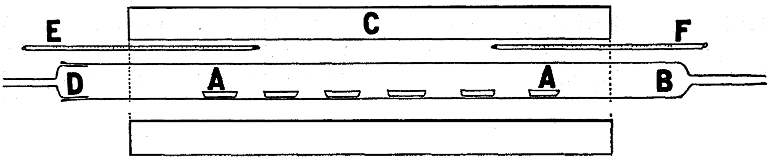

Fig. **3.**

IV. Melting Points of the Anhydrous Chlorides

In the melting point determinations the anhydrous chlorides were prepared both at normal and at reduced pressures. When prepared in the quartz reaction flask the thermocouple was in position during dehydration. In cases where the salt was prepared at reduced pressures, the anhydrous salt was transferred to the quartz reaction flask at a temperature of 200° or above.

The platinum to platinum-rhodium thermocouple with potentiometer indicator was previously calibrated in the usual manner by determining the melting points of Bureau of Standards metallic zinc and metallic aluminum and of pure metallic silver[5] prepared in this Laboratory. Finally, to insure the calibration under actual working conditions, the pyrometer was calibrated against the melting points of especially purified sodium chloride and potassium chloride. The sodium and potassium chlorides were fused under the exact conditions that were present during the fusion of the anhydrous rare earth chlorides, thus eliminating any possibility of a constant source of error.

After the dehydration, the temperature was rapidly raised until fusion of the salt occurred. Immediately upon fusion the temperature was gradually lowered and the usual time-temperature cooling curve taken. To insure check results, at least two series of dehydrations and melting point determinations were carried out on each rare earth reported. Results are tabulated.

TABLE I

DATA ON ANHYDROUS RARE EARTH CHLORIDES

Chloride	Color of fused salt	Temp. range of removal of water of hydration,[a] °C.	Values for melting point previously obtained, °C.	Values for melting point obtained by authors, °C.
$LaCl_3$	White	85 to 90	907 (1)[b]	872
		125 to 135	890 (2)[c]	872
$CeCl_3$	White	90 to 110	848 (2)	822
		165 to 190	...	822
$PrCl_3$	Light green	110 to 115	818 (1)	823
		180 to 195	810 (2)	823
$NdCl_3$	Wine red	120 to 125	785 (1)	761
		155 to 165	784 (2)	761
$SmCl_3$	Pale yellow	100 to 110	686 (1)	682
		180 to 200	686 (2)	682
$DyCl_3$	Pale olive green	110 to 130	680 (2)	655
		200 to 230	...	655
$YtCl_3$	White	110 to 120	686 (1)	624
		190 to 210	...	624
$HoCl_3$	Slight yellow tint	95 to 105	...	696
		195 to 225	...	696
$TmCl_3$	Pale yellow-green	100 to 115	...	866
		190 to 205	...	866

[a] The first value shows the temperature range in which the first five molecules of water of hydration are removed and the second value that of the removal of the last molecule of water of hydration.

[b] (1), melting point values given by Matignon.

[c] (2), melting point values given by Bourion.

Discussion

No definite explanation can be given at the present time for the variation of melting points from those given by Matignon and Bourion.

[5] Kremers, THIS JOURNAL, 40, 593, 598 (1918).

Bourion reports abnormal supercooling in the case of fused lanthanum chloride. He states that in the first reading the temperature dropped to 830° and then rose to 878°. In the second reading the temperature dropped to 836° and then rose to 880°. After heating the anhydrous chloride again, the crystallization took place between 887 and 893" and he therefore adopts 890° as the melting point of the chloride.

It was observed in the present work on the melting point of lanthanum chloride, especially, that abnormal supercooling occurred when relatively large amounts of basic salt were present. When the chloride was found to be perfectly anhydrous, supercooling in many cases was absent and never in excess of four or five degrees. The presence of small amounts of basic salt lowered the melting point of the anhydrous chloride. On the other hand, the presence of a large amount of basic chloride raised the melting point of the mixture. In the present work only those determinations in which the chlorides were perfectly anhydrous are listed.

Matignon and Bourion prepared their anhydrous chlorides by passing a mixture of chlorine and sulfur monochloride over the heated oxide. It has been suggested that there may be some sulfate formed in this manner. The presence of a small amount of sulfate would alter the melting point of the anhydrous chloride considerably.

Lack of time prevented the preparation of anhydrous chloride by the use of chlorine and sulfur monochloride.

V. Density of the Anhydrous Chlorides

The density of some of the anhydrous rare earth chlorides has been determined, usually by the pycnometer method. Due to the extremely hygroscopic properties of the anhydrous rare earth chlorides, it seemed advisable to use a method in which no liquid is necessary to contact with the anhydrous salt. The apparatus used was that described by Karns,[9] in which the displacement of a small amount of dry air from a calibrated glass chamber is recorded by the height of a column of mercury. By reference to mercury and a correction for a change in barometric pressure, it is possible to determine very accurately the density of the anhydrous chloride under fairly anhydrous conditions. This method is especially applicable when only small quantities are available, as was the case in some of the anhydrous chloride density determinations.

The mercury in the apparatus was first purified by running it through a column of nitric acid in a fine spray; it was then twice distilled under reduced pressure and finally boiled to remove all the moisture. The mercury in the apparatus, as well as that in the density chamber, was protected from the moisture of the air by drying tubes filled with anhydrous calcium chloride.

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[9] Karns, THIS JOURNAL, 48, 1176 (1926).

The values obtained for the density of the anhydrous chlorides at 25° are represented in Table II.

TABLE II

DENSITIES OF ANHYDROUS CHLORIDES AT 25°

Chloride	Previous value given	Density, found	Chloride	Previous value given	Density, found
$LaCl_3$	3.79"	3.82	$SmCl_3$	4.27"	4.30
	3.94[b]			4.465'	
$CeCl_3$	3.92"	3.97	$DyCl_3$	3.67"	3.60
$PrCl_3$	4.07"	4.15	$YtCl_3$	..	2 81
	4.017'			2.80[b]	
$NdCl_3$	4.14"	4 17	$HoCl_3$	3.80[c]	4.25
	4.195[b]		$TmCl_3$	..	4.34
	4.134[d]				

[a] Values as given by Matignon, ref. 3.
[b] Values as given by Bourion, ref. 4.
[c] Values given by Hopkins and Driggs, ref. 6 d.
[d] Values given by Baxter and Chapin, ref. 5 a.

The values for the density of the anhydrous chlorides as obtained by this method agree fairly well with those given by Matignon[3] and Bourion.[4] There are indications that the density of the powdered, anhydrous, fused chloride may vary slightly with that of the crystalline fused anhydrous chloride. In general, it seems that the density of the fused mass is somewhat lower than that of the powdered anhydrous chloride. Such a difference might occur if the fused mass contained voids and the density were determined by the liquid displacement method. The determinations here given were made by the use of coarsely powdered material.

VI. Hydrogen Ion Concentration of the Aqueous Solutions

The hydrogen ion concentrations of the aqueous solutions prepared by dissolving the anhydrous chlorides of the rare earth salts in water are of interest because of the marked degree of hydrolysis exhibited by these salts when dissolved in water.

A Leeds and Northrup Students' Potentiometer, as described in their bulletin No. 765, was used in the determination of the hydrogen ion concentration. The calomel half-cell was made from mercury thrice distilled in a vacuum, while the calomel was prepared electrolytically in the manner described by Ewing.[10] The calomel half-cell contained a saturated potassium chloride solution and was connected to the aqueous rare earth chloride solution by a salt bridge. A hydrogen electrode prepared by depositing platinum black over a gold plated platinum electrode dipped into the beaker containing the solution of anhydrous rare earth chloride. The hydrogen passed over the hydrogen electrode was obtained from a cylinder, bubbled through an alkaline pyrogallic

[10] Ewing, THIS JOURNAL, 47,301 (1925).

acid solution and then through a solution of the same vapor pressure as the solution whose hydrogen ion concentration was to be determined. After the hydrogen electrode had come to normal the electromotive force maintained between the hydrogen electrode and the calomel half-cell was measured by the potentiometer adjusted by a Weston standard cell. The hydrogen electrode was always carefully washed when a change of solutions took place to prevent any dilution of the standard rare earth chloride solution. After the hydrogen electrode had come to constant value, the electromotive force maintained between the hydrogen electrode and the calomel half-cell was determined by the potentiometer adjusted against a Weston standard cell. From this value of the electromotive force maintained in the aqueous solution of the rare earth chloride the hydrogen ion concentration expressed in PH units may be calculated by the following formula

$$P_H = 16.9\,(V = 0.246)$$

where V is the electromotive force as measured and 0.246 is the electrode potential of the calomel half-cell.

The PH values for the solutions of the anhydrous rare earth chlorides as calculated are given in Table III.

TABLE III

VALUES OF HYDROGEN ION CONCENTRATION

Chloride	Normality	E.m.f., volts	PH values	Chlorine	Normality	E.m.f., volts	Pa values
$LaCl_3$	**0.4950**	**0.4457**	**3.375**	$DyCl_3$	**0.3204**	**0.4910**	**4.140**
	.0495	.4992	4.279		.03204	.5170	4.580
	.00495	.5714	5.497		.003204	.5370	5.180
$CeCl_3$	.5780	.3225	1.293	$YtCl_3$	.2635	.3050	0.9971
	.0578	.3570	1.876		.02635	.3085	1.056
	.00578	.4033	2.659		.002635	.3450	1.673
$PrCl_3$	.3330	.4072	2.662	$HoCl_3$	.0209	.2990	0.8957
	.0333	.4756	3.880		.00209	.3280	1.386
	.00333	.5666	5.417		.000209	.3793	2.253
$NdCl_3$	.4333	.3832	2.319	$TmCl_3$	.1108	.3108	1.095
	.04333	.4138	2.835		.01108	.3492	1.638
	.004333	.4664	3.724		.001108	.4045	2.679
$SmCl_3$	.4188	.3083	1.053				
	.04188	.3396	1.582				
	.004188	.3912	2.453				

In order that the relative values determined for the hydrogen ion concentration of the various rare earth chlorides may have a greater comprehensive value, they are plotted in the following graph shown in Fig. 4. In order that the curves may be of significance, the logarithm of the PH value multiplied by the normality is plotted against the logarithm of the normality. Under these conditions, it is evident from the curves that the anhydrous chlorides of the rare earths will be completely hydrolyzed at infinite dilution.

Hopkins[11] gives the following order of decreasing basicity of the rare earths: lanthanum, cerous cerium, praseodymium, neodymium, gadolinium, samarium, yttrium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium and ceric cerium. It is evident from the curves that the results obtained follow this order rather closely with the exception of dysprosium which, from the hydrogen ion concentration values in aqueous solutions, seems to be far more basic than heretofore represented.

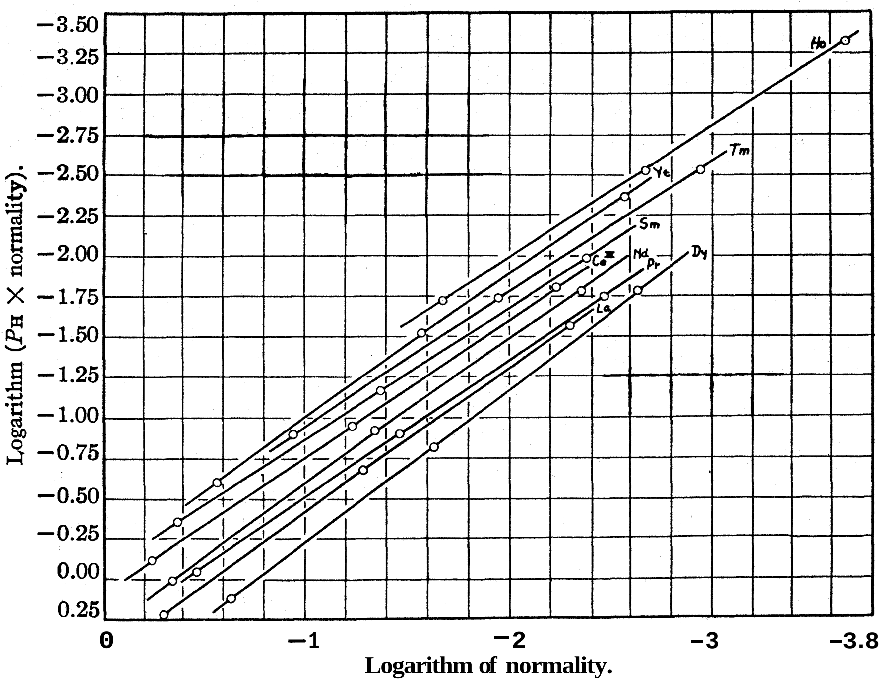

Fig. 4.—Hydrogen ion concentration of aqueous solutions of some anhydrous rare earth chlorides at 25°.

It is at this time impossible to give any explanation of this fact. The results were thrice checked and there seems to be no error which can account for the peculiarity. The values obtained are not sufficiently accurate to be taken as absolute values but show very definitely the relative hydrogen ion concentration of the aqueous anhydrous rare earth chloride solution.

VII. Summary

The anhydrous chlorides of lanthanum, cerous cerium, praseodymium, neodymium, samarium, dysprosium, yttrium, holmium and thulium were prepared by heating their hexahydrates in an atmosphere of dry hydrochloric acid gas until all of the water of hydration was expelled.

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[11] Hopkins, "Chemistry of the Rarer Elements," D. C. Heath and Co.. Boston. 1923, p. 101.

The dehydration of the hydrated rare earth chlorides was accomplished first at ordinary pressures, when the process is slow; and second at reduced pressures, when the dehydration is rapid.

The melting points of some of the anhydrous rare earth chlorides were determined in an atmosphere of dry hydrochloric acid gas by use of the cooling curve method.

The densities of some of the anhydrous chlorides of the rare earths were determined by an air displacement method.

The hydrogen ion concentration of the aqueous solutions of some of the anhydrous rare earth chlorides was determined by electrometric measurement with a hydrogen electrode.

URBANA, ILLINOIS

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

GASEOUS SOLUTIONS

BY MERLE RANDALL AND BENJAMIN SOSNICK

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There are two types of formulation of the properties of systems involving gaseous solutions, corresponding to the two types of formulation of the properties of liquid solutions. The one, recently used by Keyes,[1] requires, aside from a knowledge of the empirical constants of a selected equation of state, a knowledge of the change in the heat capacity and heat content of the gas or gases in the mixture with temperature and pressure. The other, used by Lewis and Randall,[2] determines the ratio of the fugacity of each gas in the mixture to the fugacity in a selected standard state at each temperature, and needs then only the change in the heat content of the gas in its standard state, with the temperature, to complete the ordinary thermodynamic formulation of the system.

Either type of formulation, if supplied with sufficient empirical constants, will give accurate results, but we believe that the second type leads to greater accuracy with fewer constants[3] and less labor. In this paper we shall elaborate the method of the latter authors and present the values of the fugacity of the constituents of gaseous mixtures in so far as they can be determined from the existing data. The rough regularities exhibited by these functions should be useful for estimating the values of similar functions in other undetermined systems.

In the absence of experimental information, Lewis and Randall[4] in

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[1] Keyes, THIS JOURNAL, 49, 1393 (1927).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, Chap. XVII.

[3] *See* Randall, *Trans. Faraday Soc.*, 23, 498 (1927), for a discussion of the significance of the activity coefficient.

[4] Ref. 2, p. 225.

1923 were forced to consider all gaseous solutions to be nearly perfect in the sense of their generalized statement of Raoult's law,[5] that "the fugacity of each constituent is proportional to the mol fraction of that constituent at every temperature, and at every pressure." They pointed out that it was reasonable to suppose that the solution of a given pair of substances would be more nearly perfect the less the density of the solution or, in other words, the greater the average distance between the molecules. We shall see that the deviations of such mixtures from the generalized Raoult's law are not as large as those in liquid mixtures, but that the same kinds of deviations are present.

In the case in which the solution is perfect we may write

$$f_2 = f_2^\circ N_2 \tag{1}$$

where f_2 is the fugacity in the mixture, f_2° the fugacity of the pure constituent at the same temperature and same total pressure and N_2 the mole fraction of the constituent chosen as solute. In any case the laws of the dilute solution require that this law will be the limiting law which is approached when the mole fraction of the constituent is nearly unity. These laws also require

$$f_2 = k_2^\circ N_2 \tag{2}$$

as the limiting law in the infinitely dilute solution, where k_2° is a constant which at a given temperature and total pressure is dependent upon the nature of the solute and solvent. The constant k_2° in the case of solutions is known as the Henry's law constant. The difference in the numerical value of f_2° and k_2° is greater the greater the divergence of the solution from the perfect solution. The validity of these laws has been amply proved in many cases of liquid mixtures and of solutions of gases in liquids.

Gaseous Solutions Above the Critical Temperatures of the Constituents

Gillespie[6] used the gaseous perfect solution rule and showed that the data for the ammonia equilibrium at different pressures obtained by Larson and Dodge[7] were approximately in accord with the rule. Keyes[1] assumed that for mixtures of gases the constants of his equation of state were additive, except the pressure correction term which was taken as a square root function. He also corrected for the "aggregation" of the molecules into condensed species. By laborious calculations he showed that the above data of Larson and Dodge and also of Larson[8] were in agreement with his assumption. He states that the data obtained by Burks[9] for mixtures of methane and nitrogen are also in agreement with his assumption.

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[5] Lewis, THIS JOURNAL, **30,** 668 (1908); Lewis and Randall, ref. 2, p. 222.

[6] Gillespie, *ibid.*, 48, 28 (1926).

[7] Larson and Dodge, *ibid.*, 45, 2918 (1923).

[8] Larson, *ibid.*, 46, **367** (1924).

[9] Burks, "Thesis," Massachusetts Institute of Technology, Cambridge, Mass., 1924.

The extent to which the generalized Raoult's law applies is shown in Fig. 1, in which the ratio of the fugacity of the constituent in the mixture, f, to the fugacity of the pure gas at the same total pressure, f° (or the activity referred not to the gas at unit fugacity but to the fugacity of the gas at the given total pressure), is plotted against the mole fraction. The data are taken from the computations of Gibson and Sosnick[10] from the data of Masson and Dolley,[11] for mixtures of argon and ethylene. As is to be expected the least dense gaseous mixtures at one atmosphere follow the straight diagonal lines, or lines for perfect solutions. The deviation, as shown, is greater as the total pressure is increased. The curves appear in every way to be similar to those obtained with mixtures of liquids of nearly the same polarity.[12]

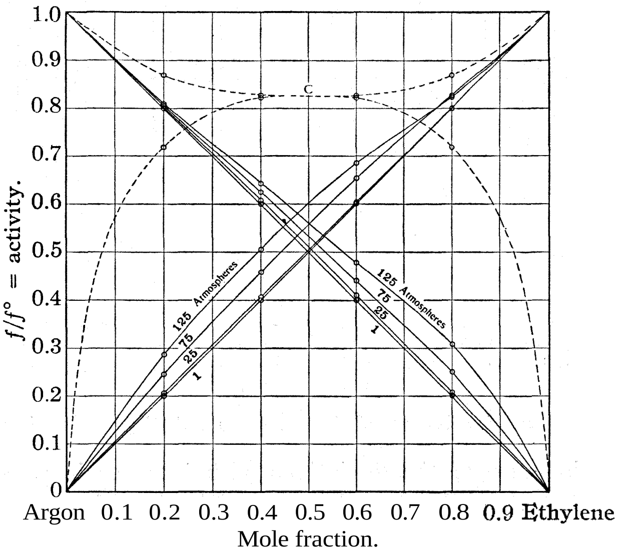

Fig. 1.—Activity of argon and ethylene in mixtures at 25°.

The deviations are better shown in Fig. 2, in which the logarithm of the activity coefficient, γ, defined as the quotient of the activity by the mole fraction, $f_2/f_2^\circ N_2$, is plotted against the mole fraction. Again it is evident that the deviations are larger the more dense the gas; but above about 100 atmosphere in solutions containing a small amount of the given constituent there is a marked decrease in the rate of increase of the deviations with pressure, and in fact an actual decrease[13] in some cases.

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[10] Gibson and Sosnick, THIS JOURNAL, 49, 2172 (1927).

[11] Masson and Dolley, Proc. Roy. Soc. (London), 103A, 524 (1923).

[12] See Hildebrand, "Solubility," Chemical Catalog Co., New York, 1924, Chap. 5.

[13] *See* Figs. 1 and *2* of ref. 10.

The individual curves of Fig. 2 resemble those of typical pairs of liquids as shown by Hildebrand.[12] He has shown[14] that practically all such curves for liquid solutions may be represented by an equation of the form

$$\ln \gamma = \ln(f_2/f_2^{\circ}N_2) = 1/RT(bN_1^2 + cN_1^3 + \ldots) \qquad (3)$$

in which the constants b, c, etc., are independent of the temperature, but vary with the pressure. In many cases an equation with the single term in b is sufficient to represent the data, but our curves cannot be fitted by a single constant equation.

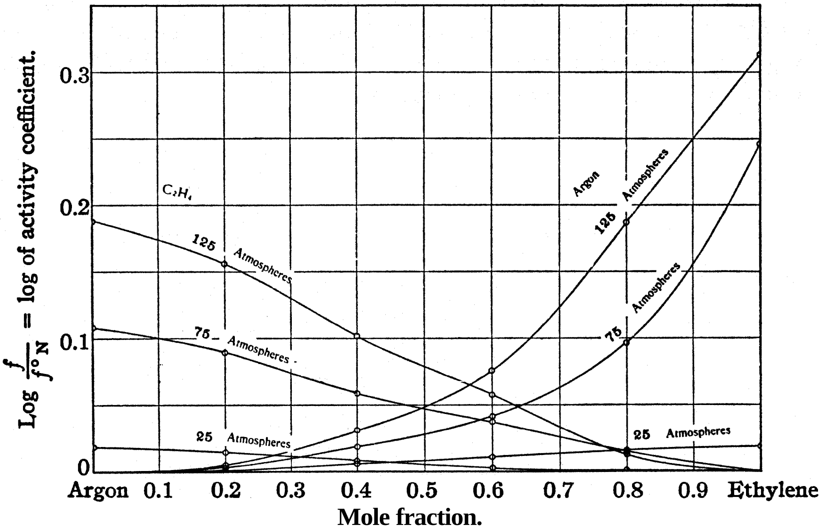

Fig. 2.—Logarithm of activity coefficient of argon and ethylene in mixtures at 25°.

Continued increase of the deviations with increase in pressure would lead to a curve such as the dotted curve of Fig. 1, which has a horizontal portion at C. In the case of liquids the point C is the critical mixing point. The dotted curve corresponds to a single constant equation with a value of b = 1185 cal. per deg. Further increase in the value of b at this temperature would then lead to the mathematical condition for the separation into two gaseous phases. However, we note in Fig. 2 that there is a falling off in the rate of increase of log γ (there is an actual decrease in some cases) as the pressure is increased and consequently a decrease in the value of b. A continued increase in the value of log γ is necessary for the coexistence of two gaseous phases in equilibrium, which, in accordance with the ordinary ideas of a gaseous phase, cannot occur.

Hildebrand[14] obtained the expression

$$(db)/(dP) = (\bar{V}_2 - V_2)N_1^2 \qquad (4)$$

for the change of value of b in the single constant equation, when the

[14] Hildebrand, *Proc. Nat. Acad. Sci.*, 13, 267 (1927).

pressure on a liquid mixture was varied at constant temperature and composition. While we are unable to make a quantitative application of this equation in the case of gases, we note that the above results are in qualitative agreement. Even when the difference in the partial molal volume of the gas and its molal volume decreases, the value of b decreases, as in the case of the argon at 125 atmospheres. The difference between the partial molal volume and the molal volume of a gas in a mixture increases as the pressure is increased but at high pressures this is no longer the case.[10] It is true that the percentage difference in these two quantities increases with pressure, but the absolute difference is smaller than at lower pressures. This again points to a value of b which will always be below that necessary for the coexistence of two gaseous phases in equilibrium,

The Fugacity of Supercooled Vapors

In the previous examples the temperature of the mixtures was above the critical points of the pure constituent gases. Before proceeding to a consideration of the vapor pressure of liquids and solids in the presence of inert gases we will study the form of the fugacity–pressure ratio of supercooled vapors. As an example we will assume that ammonia vapor obeys approximately the equation of van der Waals. The same general conclusions would be obtained by the use of the Keyes[15] equation of state, providing the constants are such as to give the critical temperature and pressure. The Keyes equation is inconvenient for calculating the ratio of the fugacity to the pressure, as we are unable to integrate the analytical expression for Vdp. A satisfactory equation of state, which would lead to an expression for Vdp which could be integrated, is much needed. An equation from which values of V could be directly calculated from those of P would enable us to utilize the graphical method of Lewis and Randall.[2] We have calculated values of P from selected values of V at 500, 405.1, 401 and 375°K., using $a = 4.1635 \times 10^6$ and $b = 37.11$ as the constants in the van der Waals' equation, which gives 405.1°K. and 112 atmospheres for the critical temperature and pressure, respectively, and at 318.1, 293.1, 273.1 and 253.1°K. from the Keyes equation[6]

$$P = 82.058\,(t + 273.13)/(V - 135.7 \times 10^{-68.24/V}) - 8.5408 \times 10^6/(V + 33.93)^2 \quad (4)$$

We have plotted the values of $\alpha = RT/P - V$ against the pressure in Fig. 3. The values of $\log (f/P)$ are given by the equation,[2]

$$\log (f/P) = -\text{area}/189.0T \quad (5)$$

where the area is taken under the curve from $P = 0$ to the given pressure. Above the critical temperature the values of α gradually increase, but at very high pressures decrease, and at still higher pressures become slightly negative. At the critical temperature the values of α rapidly increase

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[15] Keyes, *Proc. Nat. Acad. Sci.*, 3, 323 (1917).

as the pressure nears the critical pressure, at which point $d\alpha/dP$ is infinity. Beyond this point α again increases, less rapidly, reaches a maximum, then rapidly decreases and finally becomes slightly negative at the higher pressures. Below the critical temperature (Curves C and D) the value of α increases with the pressure, more rapidly in the range of supercooled vapor, until the maximum in the P-V isotherm is reached and continues to increase (dotted part of curve) as the pressure decreases with smaller molal volumes in the unstable portion. If negative pressures are not attained as we proceed along the P-V isotherm to the minimum, we find a "turning point" in the α-P curve, beyond which the curve represents the difference between the ideal molal volume of the gas and the superheated liquid. At lower temperatures (Curves E to H), where for accuracy we have used the Keyes equation, the value of α reaches infinity at $P = 0$. The negative values of $(RT/P-V)$ are meaningless until P again equals zero as we follow along the curve, and there is another branch starting at infinity for zero pressure of superheated liquid and following above the curve.

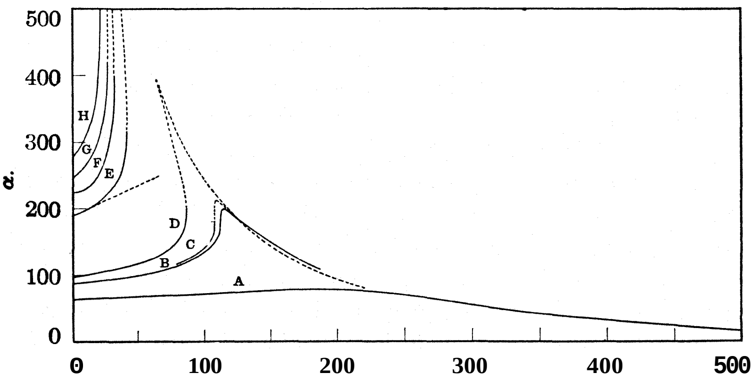

Fig. 3.—Alpha function for ammonia vapor. A at 500°, B at 405.1° (critical temperature), C at 401°, D at 375°, E at 318.1°, F at 293.1°, G at 273.1° and H at 253.1°K.

It is obvious from the curves of Fig. 3 that it is impossible to calculate the fugacity of a pure supercooled vapor above the pressure corresponding to the maximum in the P-V isotherm.

Gaseous Solutions Below the Critical Temperature of One of the Gases

Lurie and Gillespie[16] have measured the composition of mixtures of nitrogen and ammonia in equilibrium with a mixture of barium chloride and barium chloride octa-ammine at 45°. Col. 1 of Table I gives the total pressure, Col. 2 the mole fraction of ammonia in the vapor phase and Col.

[16] Lurie and Gillespie, THIS JOURNAL, 49, 1146 (1927).

3 the fugacity of the ammonia in equilibrium with the solids. We have assumed the difference in molal volumes of the solids to be 20 cc. as taken by Lurie and Gillespie and have calculated the change in activity of the solids with the pressure in the usual manner.[17] The fugacity of the ammonia vapor, given in Col. 4 for the various pressures in Col. 1, was calculated by means of Equation 5, using the plot of a against P in Fig. 3. The values in brackets for the two highest pressures were obtained by using a value of a indicated by the broken line in Fig. 3. Col. 5 gives the fugacity of the ammonia according to the rule of Lewis and Randall.

TABLE I

ACTIVITY FUNCTIONS OF AMMONIA VAPOR IN MIXTURES WITH NITROGEN AT 45°

P (atmos.)	$N_2(NH_3)$	f_2	f_2°	$f_2^\circ N_2$	k_2	k_2/f_2°	k_2/P
7.123	**1.000**	6.759	6.759	6.759	6.759	1.000	0.952
10.133	**0.7040**	6.774	9.40	6.615	9.62	1.022	.949
11.716	.6393	6.783	10.73	6.86	10.61	0.990	.906
13.272	.5655	6.791	12.02	6.88	12.05	1.003	.905
23.695	.3313	6.845	19.75	6.54	20.67	1.046	.872
32.818	.2478	6.894	25.45	6.26	27.80	1.078	.846
47.912	.1743	6.974	(32.65)	(5.69)	40.00	(1.225)	.835
60.864	.1484	7.043	(37.09)	(5.50)	47.45	(1.279)	.780

By referring to Equations 1 and 2 it is evident that the number, k, by which we multiply N_2 to obtain f_2, varies continuously from f_2°, the fugacity of the pure ammonia at the given temperature and pressure, to k_2°, the limiting value at infinite dilution, corresponding to the Henry's law constant for liquid solutions. For small mole fractions this number, k_2, will not differ appreciably from k_2°. The values of k_2 are given in

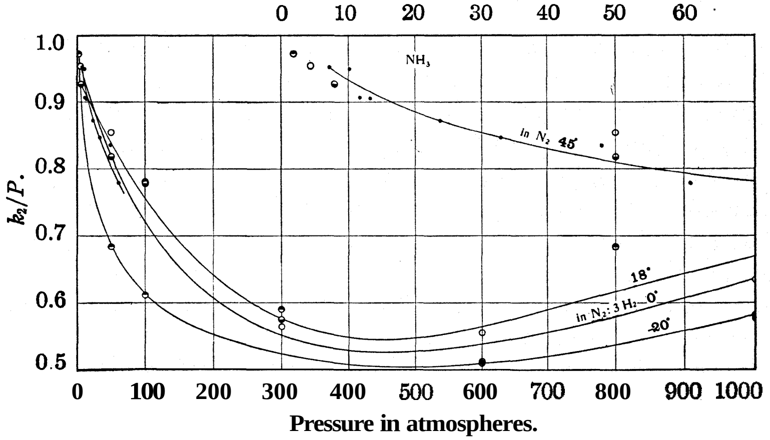

Fig. 4.—Activity function of ammonia vapor in mixtures. ● in N_2 at 45°, ◒ in N_2: 3 H_2 at −20°, ○ in N_2: 3 H_2 at 0°, ◓ in N_2: 3 H_2 at 18°.

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[17] See Lewis and Randall, ref. 2, p. 198.

Col. 6, and the ratio k_2/f_2°, given in Col. 7, is a measure of the departure of the gaseous solution from the law of the perfect solution. This ratio, k_2/f_2°, is defined as the activity coefficient in Equation 3, or is the number by which we multiply the mole fraction to give the activity referred to the activity of the pure gas at the same temperature and pressure as unity, and is in this sense analogous to the ordinary activity coefficient in solutions. The last column gives the ratio of k_2/P, which we shall find useful in studying these systems at still higher pressures. The values of k_2/P are plotted in Fig. 4.

Larson and Black[18] have studied the approximate composition of mixtures of ammonia and 1 to 3 mixtures of nitrogen and hydrogen up to 1000 atmospheres' total pressure in equilibrium with liquid ammonia at various temperatures between —22 and 20°. We have interpolated their results to —20, 0 and 18° and summarize our studies in Table II.

TABLE II

ACTIVITY FUNCTIONS OP AMMONIA VAPOR IN MIXTURES WITH 1:3 NITROGEN HYDROGEN MIXTURES

P (atmos.)	f_2 (−20°)	N_2 (−20°)	k_2/P (−20°)	f_2 (0°)	N_2 (0°)	k_2/P (0°)	f_2 (18°)	N_2 (18°)	k_2/P (18°)
v. p.	1.833	1.0000	0.972	4.045	1.0000	0.954	7.351	1.0000	0.927
50	1.946	0.0570	.683	4.271	0.1000	.854	7.716	0.1885	.818
100	2.071	.0339	.611	4.533	.0581	.780	8.174	.1050	.778
300	2.655	.0150	.590	5.753	.0340	.564	10.309	.0597	.575
600	3.858	.0126	.510	8.219	.0246	.555	14.608	.0476	.512
1000	6.344	.0109	.582	13.239	.0209	.634	23.241	.0403	.577

The vapor pressure of ammonia was taken as 1.88 at —20°, 4.24 at 0° and 7.93 atmos. at 18°, and the molal volume as 25.84 at —20°, 26.69 at 0° and 27.74 cc. at 18°. The solubility of the gases in the liquid ammonia was neglected. The fugacities of the pure ammonia at its vapor pressure were taken by aid of the curves of Fig. 3. Obviously any attempt to calculate the fugacity of pure "supercooled" ammonia vapor at the measured total pressures is meaningless. The values of k_2/P are also plotted in Fig. 4.

The recent measurements of Bartlett[19] on liquid water and compressed gases enable us to examine more accurately the limiting value of the activity coefficient in dilute gaseous solutions at higher pressures. The activity of the water is not constant at the several pressures, but can be calculated from the molal volume of the water at varying pressures.[17] The amount of gas dissolved by the water was estimated to be insufficient to lower the activity of the water by more than a few per cent.

The activity of the liquid water at the several temperatures and pressures used by Bartlett (neglecting the lowering by dissolved gases) is

[18] Larson and Black, THIS JOURNAL, 47, 1015 (1925).

[19] Bartlett, *ibid.*, 49, 65 (1927).

shown in Cols. 2 to 4 of Table III. The volumes were taken from the work of Bridgman.[20] The fugacity of the liquid water at atmospheric pressure is 0.03125 at 25°, 0.06372 at 37.5' and 0.1219 at 50°. The fugacity of the liquid water at the several pressures is shown in Cols. 5 to 7 of Table III.

TABLE III

FUGACITY OF LIQUID WATER AT VARIOUS TEMPERATURES AND PRESSURES

P (atmos.)	*a*(25°)	*a*(37.5°)	*a*(50°)	f_2(25°)	f_2(37.5°)	f_2(50°)
1	1	1	1	0.03125	0.06372	0,1219
100	1.0757	1.0728	1.0703	,03362	.06836	.13047
200	1.1576	1.1515	1.1461	.03618	.07337	.13971
300	1.2454	1.2356	1.2270	.03892	.07873	.14957
400	1.3394	1.3254	1.3132	.04186	.08445	.16009
500	1.4402	1.4214	1.4050	.04501	.09572	.17127
600	1.5481	1.5240	1.5029	.04838	.09711	.18320
700	1.6637	1.6336	1.6072	.05199	.10409	.19592
800	1.7874	1.7506	1.7184	.05586	.11155	.20947
900	1.9200	1.8755	1.8367	.06000	.11951	.22389
1000	2.0618	2.0089	1.9628	.06443	.12701	.23927

TABLE IV

ACTIVITY FUNCTION OF WATER VAPOR IN MIXTURES WITH HYDROGEN AND WITH NITROGEN AT 50°

P (*atmos.*)	*Ne* in *Ha*	k_2 in *Ha*	k_2/P in H_2	*Np* in N_2	k_2 in N_2	k_2/P in N_2
100	0.1391	93.8	0.938	0.1576	82.8	0.828
200	.0785	178.0	.890	.1001	139.6	.698
300	.0582	257.1	.857	.0796	188.0	.627
400	.0473	338.7	.847	.0684	234.1	.585
500	.0408	420.0	.840	.0623	275.0	.550
600	.0364	504.0	.840	.0584	318.0	.530
700	.0334	586.5	.838	.0551	355.6	.508
800	.0312	671.5	.839	.0527	397.4	.497
900	.0294	761.0	.845	.0505	443.0	.492
1000	,0282	849.0	.849	.0486	493.0	.493

TABLE V

ACTIVITY FUNCTION OF WATER VAPOR IN MIXTURES WITH 3:1 HYDROGEN–NITROGEN AT 25, 37.50 AND 50°

P (atmos.)	N_2 (25°)	k_2 (25°)	k_2/P (25°)	N_2 (37.5°)	k_2 (37.5°)	k_2/P (37.5°)	N_2 (50°)	k_2 (50°)	k_2/P (50°)
100	0.0385.	87.3	0.873	0.0768	89.0	0.890	0.1451	89.9	0.899
200	.0234	154.7	.773	.0449	163.3	.817	.0846	165.0	.825
300	.0183	212.5	.708	.0341	230.9	.770	.0631	237.1	.790
400	.0157	266.8	.667	.0287	294.1	.735	.0521	307.2	.768
500	.0140	321.5	.643	.0254	377.0	,724	.0460	372.5	.745
600	.0128	377.8	.630	.0231	420.0	.700	.0417	439.5	.732
700	.0120	433.0	.619	.0214	487.0	.696	.0386	508.0	.726
800	.0113	494.5	.618	.0200	558.0	.697	.0362	579.0	.724
900	.0108	556.0	.618	,0189	632.0	.702	.0344	651.0	.723
1000	.0104	620.0	.620	.0181	702.0	.702	,0328	729.0	.729

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[20] Bridgman, *Proc. Am. Acad. Arts Sci.*, *47*, 439 (1912).

The various values of N_2, of k_2 found by dividing f_2, from Table I, by N_2 and of k_2/P are given in Tables IV and V for the various gases studied by Bartlett.

Since the attempt to calculate the fugacity of the supercooled water vapor at the pressures used by Bartlett is meaningless, as was shown in the case of ammonia vapor, we cannot calculate the activity coefficient referred to the pure supercooled gas. We show the values of k_2/P in Fig. 5 for the various mixtures at different pressures. The curves necessarily begin at the activity coefficient (f/P) of the pure gas at its vapor pressure. The value of k_2/P depends upon the added gas, decreases with increase in pressure, less rapidly in the region of a few hundred atmospheres, remains about constant for a considerable range and then slowly increases.

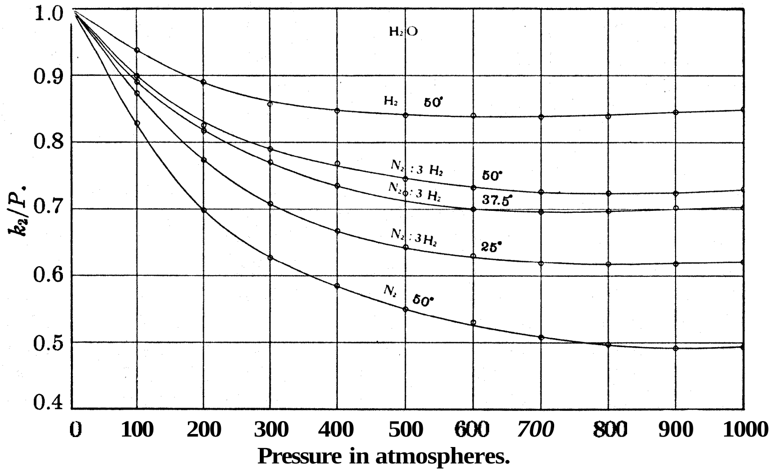

Fig. 5.—Activity function of water vapor in mixtures.

The curves of Figs. 4 and 5 also represent approximately the quotient of the limiting value k_2° by P. It is significant that the value of k_2/P reaches a minimum value in every case, corresponding, perhaps, to the limiting value of log γ for argon in Fig. 2. The values of k_2/P are not far different from what we would expect for the ratio of Raoult's and Henry's law constants for mixtures of liquids of similar likeness.

The considerations of this section limit the application of the Lewis and Randall rule to vapors above their critical point, and to a limited extent below the critical point. The values of the ratio k_2/P, however, for any given pressure, show how the fugacity of the gas depends upon the chemical nature of the added gases, and these ratios furnish an excellent means of estimating the effect for other temperatures, pressures and other gases.[21]

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[21] k_2/P is in a sense an activity coefficient, for it represents the number by which we multiply the product of the mole fraction and the total pressure of the gases to obtain the actual fugacity or activity of the gaseous constituent.

It is possible to make a rough estimate of the value of $f_2°$ for high pressures and for temperatures below the critical point by extrapolating the values of $f_2°$ for a given pressure obtained at higher temperatures to the lower temperature. This, in effect, partially leaves out of consideration the effect of the attraction terms in the equation of state. As a matter of fact we should not expect the attraction between atoms of the same kind in these dilute solutions to be a function of the attraction between their own molecules so much as of that between the solute and solvent molecules. In fact, the highest temperature for the formation of a liquid phase is usually lowered by the addition of a gas with a lower critical point.[22] The calculations of Lurie and Gillespie,[16] in effect, take this into consideration.

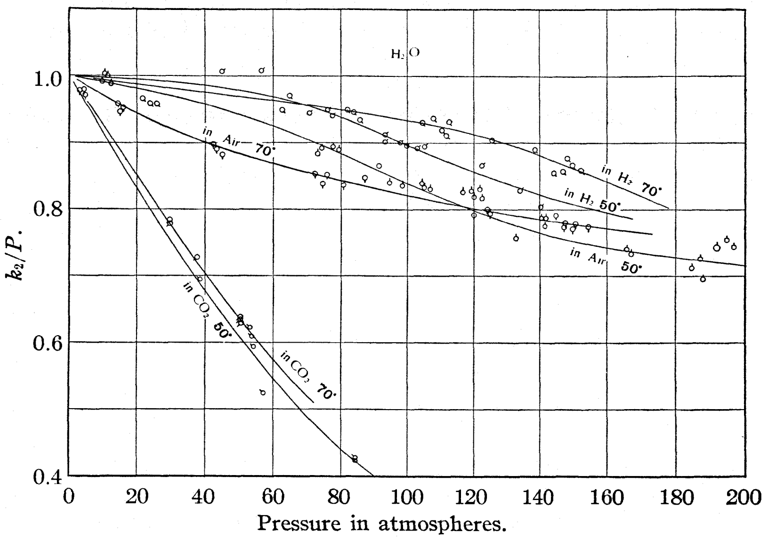

Fig. 6.—Activity function of water vapor in mixtures.

Pollitzer and Strebel[23] determined the concentration of water vapor in the presence of air, of hydrogen and of carbon dioxide up to about 200 atmospheres at 50 and 70°. Their method was less accurate than that of Bartlett, but from their results the same conclusions can be drawn. In the case of the solutions in carbon dioxide, a small correction was made for the effect of the solubility of the carbon dioxide in the liquid phase. This amounted to less than 2% in the largest case. We shall not reproduce our calculations but give in Fig. 6 the values of k_2/P plotted against P as in Fig. 4. As we might predict from the imperfectness of carbon dioxide as a gas at these temperatures the effect upon the activity of the water vapor is much larger than that of the other more perfect gases.

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[22] *See* Caubet, "Liquefaction des Melanges Gazeux," Hermann, Paris, 1901.

[23] Pollitzer and Strebel, *Z. physik. Chem.*, **110**, 768 (1924).

Pollitzer and Strebel[23] also determined the composition of mixed gases in equilibrium with liquid carbon dioxide at 221.5 and 273.1°K. The compressibility of liquid carbon dioxide was assumed to be negligible, and the solubility of the nitrogen or hydrogen in the liquid was neglected. These assumptions involve a small error in the activity of the liquid. The molal volume was taken as 38 cc. at 221.5' and 48 cc. at 273.1'. The activity of the liquid is given in Col. 5 of Table VI. The vapor pressure of the liquid at 221.5°K. is about 6.6 atmospheres and at 273.1°K. is about 34.3 atmospheres. The vapor pressure was taken as the geometrical mean of the fugacity and the theoretical pressure calculated by the gas law.[24] Using the values 2522 cc. and 458 cc. for molal volumes of saturated gaseous carbon dioxide at 221.5 and 273.1°, respectively, we find the fugacity of the liquid referred to the gas at unit

TABLE VI

ACTIVITY FUNCTION OF CARBON DIOXIDE IN NITROGEN AND IN HYDROGEN

Temp., °K.	Gas	P	N_2	a_2 (1)	a_2/N_2	f_2/N_2	k_2/P
221.5	N_2	40.6	0.222	1.086	4.89	29.55	0.728
		60.5	.182	1.133	6.22	37.60	.621
		74.6	.176	1.167	6.63	40.07	.537
		78.4	.176	1.176	6.68	40.35	.515
		92.9	.179	1.212	6.77	40.90	.440
		108.4	.188	1.252	6.66	40.25	.371
		122.0	.200	1.289	6.44	38.93	.319
		125.8	.205	1.299	6.33	38.28	.304
		139.9	.230	1.338	5.82	35.13	.251
		143.2	.237	1.347	5.68	34.34	.240
		146.6	.248	1.357	5.47	33.05	.225
		148.6	.256	1.364	5.33	32.19	.216
		153.4	.270	1.376	5.10	30.80	.201
	H_2	78.4	.120	1.176	9.80	59.15	.755
		95.3	.105	1.218	11.60	70.08	.736
		100.6	.101	1.232	12.20	73.7	.733
		112.8	.094	1.264	13.45	81.2	.720
		157.3	.084	1.387	16.50	99.8	.634
273.1	N_2	53.7	.744	1.12	1.50	36.0	.67
		63.9	.668	1.12	1.68	40.3	.63
		65.1	.665	1.15	1.73	41.5	.64
		68.2	.642	1.16	1.81	43.4	.64
		75.8	.616	1.17	1.90	45.6	.60
		76.5	.615	1.18	1.92	46.1	.60
		81.9	.603	1.19	1.98	47.4	.58
		88.6	.594	1.21	2.04	48.9	.55
	H_2	78.4	.594	1.18	1.99	47.8	.61
		92.4	.534	1.22	2.29	54.9	.60
		103.0	.503	1.24	2.47	59.3	.58
		122.0	.458	1.30	2.84	68.1	.56

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[24] See ref. 2, p. 198.

activity to be 6 atmospheres at 221.5°K. and 24 atmospheres at 273.1°K. The constants in Col. 6 are those referred to the liquid at unit activity, while the ratios in Col. 7 are obtained by multiplying the ratios of Col. 6 by the fugacity of the liquid referred to the gas at unit activity. Col. 8, k_2/P, is obtained by dividing Col. 7 by the respective pressures.

The values of k_2/P from Table VI are plotted in Fig. 7. The solid circles are the values of the ratios of f_2/P at the vapor pressure of the pure liquid. The values of $f_2{}^\circ/P$ are smaller as the pressure increases, therefore a curve of $k_2/f_2{}^\circ$ would start at unity at the vapor pressure and remain nearly constant. The generalized Raoult's law appears to be of more general applicability in the case of the mixtures of carbon dioxide and nitrogen or hydrogen than in the case of mixtures of water vapor with these gases.

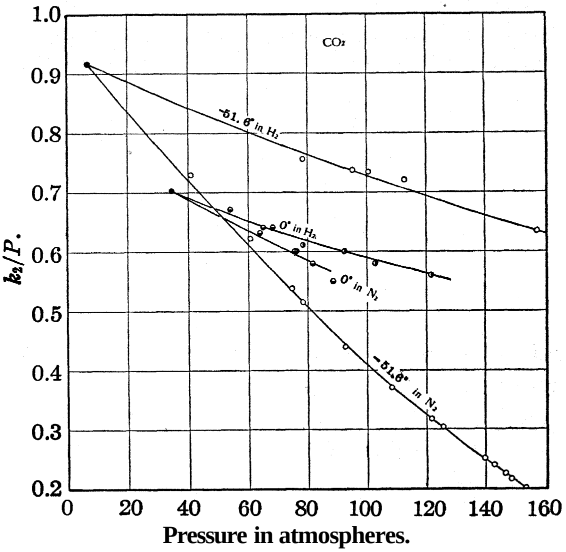

Fig. 7.—Activity function of carbon dioxide in mixtures.

Pollitzer and Strebel[23] also quote some experiments of Kölliker with mixtures of hydrogen and nitrogen in equilibrium with liquid nitrogen, but there are not sufficient data to make an interpretation on the basis here presented.

McHaffie[25] has defined a quantity, called by him the relative activity coefficient, f_p, by means of the equation

$$\log f_p = Pv_s/RT + \log c_0 - \log c_p \qquad (6)$$

in which P is the "partial pressure" of the indifferent gas, v_s the molal volume of the liquid in the condensed phase, c_0 the concentration of vapor when the liquid is under its own vapor pressure, and c_s the concentration

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[25] McHaffie, *Phil. Mag.*, [7] 1, 561 (1936); 3, 497 (1927).

of the vapor when the partial pressure of the indifferent gas is P. We have defined the activity coefficient as the number by which the mole fraction is to be multiplied to obtain the activity. Our definition conforms to the usual practice in the case of liquid or solid phases. The standard state of a liquid at each temperature is taken as the liquid under 1 atmosphere pressure. We have taken the standard state of the vapor as the vapor at unit fugacity, which is more useful for a consideration of the general problem of gaseous solutions.[26] The activity of the vapor in equilibrium with the liquid is not given by the first term on the right of Equation 6, nor is the concentration (moles per liter) of the vapor in the compressed phase its mole fraction. To call McHaffie's function an activity coefficient is, therefore, somewhat misleading. He measured quantities from which results similar to those of Bartlett can be calculated for mixtures of water vapor in equilibrium with liquid water or anhydrous and hexahydrated sodium sulfate and air to 100 atmospheres. His results are anomalous but in qualitative agreement with those of Bartlett.

Summary

The application of the generalized statement of Raoult's law to gaseous solutions has been elaborated. The deviations are found to be of the same nature but, in general, of less magnitude than those of typical liquid pairs of like polarity.

The fugacity of supercooled vapor has been investigated. It is shown that for pressures near that of the turning point of the pressure–volume curve, the fugacity of the pure constituent should not be used for the Lewis and Randall rule.

This latter rule has been shown to hold as an approximation and as a limiting law for gaseous solutions above the critical temperature of the gases, and for a limited range of total pressures for the solute gas below its critical temperature.

For solute gases below their critical temperature, values of "activity coefficients" have been calculated which enable rough quantitative predictions of values in other mixtures and at other temperatures to be made.

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[26] *See* Ref. 2, Chap. XXII, for a discussion of the definition of these quantities.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WARSAW]

THE ANALYSIS OF MIXTURES OF ETHYL ALCOHOL, ETHYL ACETATE, ACETIC ACID AND WATER

BY S. POZNANSKI

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Determination of Alcohol by Chemical Methods

In the course of work on another problem it became necessary to determine accurately the alcohol content of mixtures of not over a few tenths of a cc. The determination of the alcohol content of such a small quantity of a mixture of volatile compounds, especially if four ingredients are present, must be carried out chemically rather than by physical methods, and in order to find the best method it was necessary to compare all known methods with regard to their accuracy.

Review of the Literature

One direct method for determining alcohol is by oxidation with potassium dichromate and sulfuric acid.[1] The error resulting from the partial oxidation of alcohol to carbon dioxide is considerable in any method using potassium dichromate, but if careful blank tests are carried out the process is applicable.[1j,2] The excess potassium dichromate may be determined by titration with ferrous ammonium sulfate,[1m,n,3] or by iodimetry.4 Kuriloff and SzebQenyi determined total alcohol plus ethyl acetate in mixtures and found the ester content by saponification. The free alcohol is obtained by difference. Kuriloff's modification seems to be more exact than that of Szebérenyi. Potassium permanganate may be used as the oxidizing agent.5

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[1] (a) Bodlander, *Arch. ges. Physiol.* (*Pflügers*) 32,398 (1883); (b) Nicloux, *Compt. rend. soc. biol.,* (10) 3,841, 1126 (1896); (c) *Ann. chim. anal. chim. appl., 1,* 438 (1896); (d) Nicloux and Bauduer, *Bull. soc. chim.,* (3) 17, 424 (1897); (e) Bordas and Raczkowski, *Compt. rend. soc. biol.,* (10) **3,** 972 (1896); (f) *Compt. rend.,* 123, 1071 (1896); (g) Pozzi-Escot, *Ann. chim. anal. chim. appl.,* 7, 11 (1902); (h) 9, 126, 259 (1904); (i) Nicloux, *ibid.,* 9, 214 (1904); (j) Landsberg, *Z. physiol. Chem.,* 41, 505 (1904); (k) Nicloux, *ibid.,* 43, 476 (1904–5); (l) Widmarck, *Skand. Arch. Physiol., 35,* 125 (1917); (m) Yamakami, *Tôhoku J. Exptl. Med.,* 4, 276 (1923); (n) *Ber. ges. Physiol. exptl. Pharmakol.,* 24, 106 (1924).

[2] Thorpe and Holmes, *J. Chem. Soc.,* 85, 1 (1904).

[3] (a) Reischauer (1866), quoted by Rose, *Z. angew. Chem.,* 1, 31 (1888); (b) Benedict and Norris, THIS JOURNAL, 20, 293 (1898); (c) Cotte, *Revue internationale des falsifications,* 10,206 (1897); (d) Martin, *Mon. sci.,* (4) 17, 570 (1903); (e) Pringsheim, *Biochem. Z.,* 12, 150 (1908).

[4] (a) Bourcart, *Bull. soc. ind. Mulhouse,* 558 (1889); abstracted in *Z. anal. Chem..* 29, 604 (1890); (b) Kuriloff, *Ber.,* 30, 741 (1897); (c) Szebérenyi, Z. *anal. Chem.,* 53, 683 (1914).

[5] (a) Rose, Z. *anal. Chem., 1,* 31 (1888); (b) Herzog, *Ann.,* 351, **263** (1907); (c) Barendrecht, *Z. anal. Chem.,* 52, 167 (1913).

In Zeisel's method[6] the alcohol is converted to ethyl iodide and the iodine determined as silver iodide. The ethyl iodide may be decomposed and determined by iodimetry.[7] The ethyl alcohol may be converted into iodoform, the iodine fixed as potassium iodide and determined by precipitation with silver nitrate, the excess silver nitrate being titrated.[8] Still another procedure is to convert the alcohol to ethyl nitrite, treat with potassium iodide and determine the iodine.[9] By the method of Grün and Wirth[10] the alcohol is esterified with laurinyl chloride and the excess decomposed with water. The ester is then extracted and determined by saponification. If an ester is present along with the alcohol, this process gives the combined content of ester and alcohol. A procedure given by Wolff[11] involves esterification with acetic anhydride, which is open to the same objection as laurinyl chloride. Wolff esterified 0.5 g. of approximately 90% alcohol with 1 cc. of acetic anhydride by heating them in a sealed tube for an hour in boiling water. The tube was then placed in a bottle containing about 50 cc. of water and broken by shaking. The bottle and contents were then heated for half an hour on a water-bath at 50°. In this way the excess of acetic anhydride was converted into acetic acid, which was then exactly neutralized, phenolphthalein being used as indicator. The ester was determined by saponification with potassium hydroxide. In two analyses given the result was too small by 0.7–1.0%. The method was not applied to mixtures.

Experimental

Two methods were chosen, the one used by Bourcart and Kuriloff and that of Wolff, the former as already used with supposedly great accuracy for determining alcohol in mixtures with ethyl acetate, the latter as suitable, when conveniently modified, for the determining of free alcohol when mixed with ester, which was impossible by any procedure previously followed. Some other methods are delicate but not accurate.

Bourcart-Kuriloff Method.—The following procedure gave the best results. Forty cc. of 0.18 *N* potassium dichromate solution, 4.5 cc. of sulfuric acid (1:5) and a weighed quantity of mixture containing 0.05–0.07 g. of alcohol or about 0.11 g. of ester were placed in a 200cc. flask with a tied-in, air-tight stopper and kept at 100° (in steam) for five to six hours. The flask was then cooled and the contents and washings were poured into a glass stoppered, narrow necked, liter volumetric flask containing about 100 cc. of 1.8% potassium iodide solution, 150 cc. of water and 30 cc. of 1:5 sulfuric

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[6] (a) Prunier, J. *pharm.*, 29, 407 (1896); (b) an abstract in Z. *anal. Chem.*, 35, 218 (1896); (c) Stritar, *ibid.*, 42, 579 (1903); (d) *Z. physiol. Chem.*, **50**, 22 (1906).

[7] (a) Klemenc, *Monatsh.*, 34, 901 (1913); (b) Ripper and Wohack, Z. *landw. Versuchsw.*, 20, 102 (1917); (c) Wohack, "Handbuch der biologische Arbeitsmethoden," 1921, I, 3/3, pp. 547–552.

[8] Villedieu and Hébert, J. *pharm. chim.*, (7) 15, **41** (1917).

[9] Fischer and Schmidt, *Ber.*, 59, 679 (1926).

[10] Grün and Wirth, Z. *deut. Öl- Fett-Ind.*, 41, **145** (1921).

[11] Wolff, *Chem. Umschau Fette, Oele, Wachse Harze*, **29**, **2** (1922).

acid. After mixing, the liquid was covered with about 125 cc. of water to prevent evaporation of iodine and the flask was stoppered and allowed to stand for half an hour. The stopper and neck were then rinsed into the flask and a recently standardized, 0.1 N sodium thiosulfate solution was run in with continuous shaking, hydrated starch indicator being added when near the end-point. The sodium thiosulfate was standardized by means of an exactly 0.1 N solution of potassium dichromate, freshly prepared from dried Kahlbaum's $K_2Cr_2O_7$ "mit Garantie 99.97%." The 0.18 N potassium dichromate solution was standardized by means of the sodium thiosulfate solution in the following manner. Forty cc. of the dichromate solution and 4.5 cc. of 1:5 sulfuric acid, after heating for five to six hours (see below), were poured into a mixture of 150 cc. of 1.8% potassium iodide solution, 225 cc. of water and 45 cc. of sulfuric acid (1:5). After mixing, the liquid was covered with 150 cc. of water and titrated after standing for half an hour. Preliminary tests showed that the titer of a quantity of dichromate solution, after heating with sulufric acid as in the oxidation reaction, is lowered by about 1%. This error can be allowed for by using a correction derived from blank runs.

The content of free alcohol found was too large by 0.15–0.5%. The average value found in four determinations of ethyl acetate was 100.0%, the average deviation being ±0.4%. Such discrepancies (considerably larger than Kuriloff supposed) in mixtures containing a large amount of ethyl acetate, as did those analyzed, would give an error of many per cent. in a determination of free alcohol. Therefore, although this method is considerably more accurate than any other chemical method for the determination of alcohol, another procedure was used which is less exact in direct analyses but is suitable for the determination of alcohol in the presence of ester.

Acetic Anhydride Method.—In this process, which is acidimetric, a weighed amount of acetic anhydride is allowed to react with a known weight of alcohol or alcoholic mixture. The reaction may proceed according to either or both of the following reactions

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOH + CH_3COOC_2H_5$$
$$(CH_3CO)_2O + 2C_2H_5OH \longrightarrow 2CH_3COOC_2H_5 + H_2O$$

but the result is the same in either case. The process may be used with mixtures containing considerable water by employing approximately double the amount of acetic anhydride necessary to combine with the alcohol and water. A relatively large amount of acetic anhydride should be used in any case, especially if the composition of the mixture under analysis is unknown. The excess of acetic anhydride is decomposed with water, care being taken not to hydrolyze any of the ester, and the acetic acid produced is determined by titration.

Procedure.—The reaction is carried out in a Pyrex bulb with a capillary tube at least 5 cm. long. The bulb is weighed and then 0.15–0.4 g. of acetic anhydride is placed in the bulb by means of a capillary pipet. The capillary tube is sealed off and the bulb and contents, with the piece removed in sealing, are weighed. The end of the capillary is then broken off, 0.02–0.04 g. of alcohol or alcoholic mixture is added, the capillary sealed and the whole again weighed with the pieces of capillary tube. The bulb and contents are heated in boiling water for an hour. After cooling, the liquid in the capillary is driven back into the bulb with a small flame and the capillary carefully opened. Enough distilled water (0.04–0.1 cc.) to decompose the excess anhydride is introduced from a capillary pipet, the capillary is again sealed and the bulb with contents heated in boiling water for twenty minutes. This length of heating is sufficient to decompose the anhydride without hydrolyzing any of the ester. The bulb is then placed in a flask containing carbon dioxide free water, broken and the acetic acid titrated, taking care not to use an excess of base in order to avoid hydrolyzing any of the ethyl acetate.

The purity of the "Merck" acetic anhydride used in this investigation was determined by the above procedure. The average of the determinations on the pure anhydride was 98.63%, and the average deviation of all determinations, during four months, from the mean was ±0.2%. The method gives no indication as to the nature of the 1.4% of impurity. In all probability it was water, combined as acetic acid. If such was the case, the reagent contained only about 90% of acetic anhydride, but this is of no consequence in the analysis provided an excess is used.

The content of alcohol is calculated from the difference between the amount of acetic anhydride taken and the amount equivalent to the acetic acid found in the reaction mixture, so any error in the value for the alcohol is several times greater than the error in the anhydride. The percentages of alcohol were found to average **3%** too low (−6.4– +1.1%). The varying content of water made it impossible to use quantities of anhydride equivalent to the amount of alcohol taken. Therefore, the average deviation of parallel determinations of alcohol in proportion to itself (but not to the whole quantity of mixture) increased, with diminishing alcohol content, from ±0.5% at 40% of alcohol to ±5% when 1.5% of alcohol was present; but in the whole quantity of mixture it was always about ±0.2%. If a mixture contained free acetic acid this, of course, was determined separately.

Determination of Ethyl Acetate.—Chemically pure ethyl acetate was prepared by repeated fractional distillation in the presence of phosphorus pentoxide, and was weighed in sealed Pyrex bulbs. The best results were obtained by hydrolyzing the ester at 60–65° for fifteen to twenty hours with twice the calculated amount of barium hydroxide solution. The average deviation was ±0.09%, the results generally being slightly too high (mean 100.17%).

Determination of Acetic Acid.—In the accurate titration of acetic acid, using phenolphthalein as indicator, carbon dioxide must be carefully excluded. Carbon dioxide free distilled water is used in making up the solutions of barium hydroxide and the hydrochloric acid which is used as a run-back for any excess of base. All flasks, burets, bottles, etc., are filled with carbon dioxide free air and carbon dioxide free air is drawn through solutions which are being titrated. Volumes are read with an accuracy of 0.01–0.02 cc. on standardized burets and corrected for temperature. Benzoic acid was used as a standard and was dissolved in carbon dioxide free alcohol, it having been found that the amount of alcohol used had no effect on the results. Chemically pure, anhydrous glacial acetic acid was employed and was weighed in sealed Pyrex bulbs with an accuracy of 0.03–0.05 mg. The results obtained with this acid showed that the process was sufficiently accurate for the purpose. The influence of the barium acetate on the neutralization point, even in the absence of barium chloride, was neglected. The average deviation was found to be ±0.07%.

Micro Titration of Acetic Acid.—In the analysis of mixtures it was desirable to minimize the relative error of determining each substance. An error of 0.2–0.3% in the quantity of mixture taken is permissible in the determination of alcohol or ethyl acetate when they are the main ingredients, but since acetic acid (except in two analyses) was present only to the extent of 0.25–1.9%, it was necessary to reduce the error to some hundredths or thousandths of one per cent. To attain this accuracy, a micro method was necessary, since not more than 0.1–0.2 g. of mixture could be taken. Hence the acid had to be determined with an accuracy of some hundredths of a milligram.

Micro acidimetry, as generally used, is a delicate but not very accurate proceeding. The ability to work in a closed space is an important advantage of the apparatus of Pilch,[12] which consists of two micro burets with horizontal tubes at the lower ends which are sealed into the sides of a sphere of some 20cc. capacity. At the top the sphere has a long neck with a glass stopper for the introduction of material to be titrated, and at the bottom an outflow tube. Both side tubes and the outflow tube have stopcocks very close to the sphere so as to avoid any large amount of dead liquid space in the tubes. The side stopcocks permit additions of standard solution in as small amounts as 0.001 cc. The upper ends of the burets are fastened to a board by means of a string. Stirring is effected by shaking the whole apparatus.

When somewhat modified, the apparatus was used for determining acetic acid. The dead spaces in the side tubes were eliminated by lengthening both tubes into the sphere, as shown in Fig. 1. In this way only that part of the solution which actually flowed from the tips was used in the titration. During the titration the liquid was continually agitated so as to rinse the tubes and wash in any small drops adhering to the tips Diffusion from the solution in the tubes during the moments of rinsing was negligible, and even when the ends of the tubes were covered, as was the case in several titrations, the results did not differ from those in which they were not. The dead space in the lower tube was filled with carbon dioxide free distilled water. This water remained neutral throughout the reaction, as is shown by the fact that it exhibited no color even during the vigorous agitation of an intensely pink solution above it.

Care was taken to avoid contamination from carbon dioxide during micro titration. The neck of the sphere was short and fitted with a ground in stopper with a small air

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[12] Pilch, *Monatsh.*, 32, 21 (1911); see also Emich, "Lehrbuch der Mikrochemie," Wiesbaden, 1911, pp. 8–10.

channel. The burets were filled through side tubes connected with the solutions, which were stored in liter bottles. The burets were of 2cc. capacity, graduated to 0.02 cc. and were read (after several minutes' drainage) to 0.002 cc. Above the scale the burets were enlarged into bulbs the tops of which were protected with soda lime tubes. Portions of solution which had been in the burets for a day or more were rejected, and the standard solutions (barium hydroxide and hydrochloric acid) were not kept for more than a few weeks, as it was found that the titer changed slowly on standing. The solutions were always shaken and standardized before using. Before titration the sphere was filled with carbon dioxide free air and then 5–20 cc. of carbon dioxide free water and 2–3 drops of 0.03% phenolphthalein were introduced. During the titration the sphere was placed before a white background in order to facilitate the observing of the end-point (very pale pink color). An accuracy of 0.005–0.01 cc. of 0.01 N barium hydroxide solution could be attained.

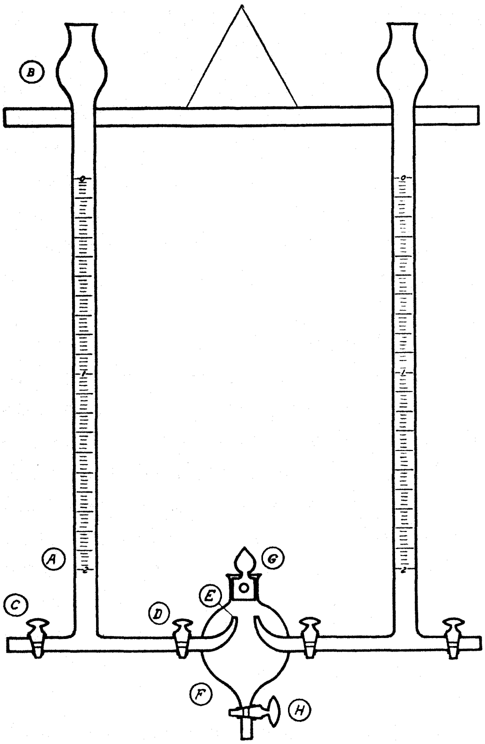

Fig. 1.

Titrations were always begun by determining the correction for the acidity of the water, that is, the smallest amount of barium hydroxide solution which would produce a faint pink color in 1 cc. of carbon dioxide free water. In practice this was done by adding alkali to 10–20 cc. of pure water until a faint pink appeared. The volume of the liquid was then ascertained by measuring it in a graduated cylinder. The correction as found from several concordant determinations was equivalent to 0.0015–0.0020 cc. of 0.01 N barium hydroxide solution. In all later analyses, both in standardizing and in actual analysis, the final volume of liquid was measured and the correction subtracted. This correction eliminates any error which might result from a difference in volumes of the solutions.

A solution of hydrochloric acid was used as a run-back and was standardized against the barium hydroxide. The barium hydroxide was compared with a determinate solution of acetic acid, the comparison being carried out as follows. Approximately 0.10–0.12 g. of chemically pure glacial acetic acid was weighed out in a sealed Pyrex bulb. The bulb was then placed in a small cylinder with carbon dioxide free distilled water, broken and the solution diluted to 100 cc. in a measuring flask. This solution was always made up just before use as colonies of microorganisms were observed in a solution which had been allowed to stand for a week. One cc. of this acid was taken in a carefully calibrated, 1cc. pipet and run into the titrating sphere, which already contained a small amount of water and indicatar. The stopper was then inserted and the titration begun. This method has the advantages that the acid and base dissociate about equally in solution, the titer of the 0.01 N barium hydroxide solution used is in strict proportion to that of the 0.1 N solution actually standardized, and the neces-

sary accuracy is obtained without a micro balance. For the determination of acetic acid in unknown mixtures, several hundredths of a gram (in one case 0.1–0.2 *g.)* of the unknown is weighed in a glass bulb. The bulb is then broken in carbon dioxide free water in a cylinder and the solution and washings are poured into the titrating sphere, water and phenolphthalein already having been placed in it. Control tests carried out with pure ethyl acetate showed that acid could be titrated with 0.01 N barium hydroxide in the presence of ester with no observable hydrolysis, provided the solution is shaken and excess of base is avoided.

Determinations showing any great deviation from the normal (not rare in the case of micro titration) were rejected. The mean of the average deviation of all series of parallel titrations was ±1.0% in standardizing hydrochloric acid, ±0.8% in standardizing barium hydroxide solutions and ±1.4% in the determination of acetic acid in unknown mixtures. When known quantities of acid were determined the average results in four mixtures, in proportion to acid content, were 1.7–2.8% too high (in one case too high by 4% and in another 2.4% too low). These errors, and also deviations from the mean values (mentioned above) in proportion to the quantity of mixture, were equal to 0.02–0.08% (in one case +0.16%) when 3–4% of acid was present; 0.003–0.007% with 0.25% of acid.

The mixtures analyzed were not in equilibrium and some changes in composition during analysis could therefore occur. Such changes, however, would produce no error in the process as long as the free acetic acid was determined immediately. In calculating the content of ester from the results of the saponification, the initial content of acid, of course, is allowed for, and even though some hydrolysis may have taken place the content of acid in the solution could not change. The same is true in the case of the alcohol. Esterification or hydrolysis would change the amount of acetic anhydride used up, but would produce an equivalent change in the amount of acid found.

The content of water was found by difference. The error in its determination, in proportion to the whole amount of mixture, would be obtained by adding (with the right signs) the errors in determining ester and alcohol and reversing the sign of the sum (the error in determining acid is very small in proportion to the amount of mixture). The maximum error may be found approximately from the average deviation in alcohol content. In general it was about 0.2% of the mixture. With an error in the content of ethyl acetate, if both were of the same sign, it would not be more than approximately 0.5%. In the least favorable of all the cases in which the methods were applied, with only 6.7% of water, the relative error was several per cent. It would be even greater if mixtures containing smaller amounts of water were analyzed.

Complete Analysis of a Known Mixture.—In order to test the accuracy of the separate determinations, a complete analysis was made of a mixture containing all four ingredients. The following results were obtained.

TABLE I

RESULTS OF COMPLETE ANALYSIS

	Acid, %	Alcohol, %	Ester, %	Water, %
Taken	0.253	9.74	81.61	8.40
Found	0.260	9.69	82.00	8.05

The author wishes to express his indebtedness to Dr. W. Swietoslawski, Professor at the Polytechnical School in Warsaw, both for suggesting this study and for his benevolent support in pursuing it.

Summary

1. The methods given in the literature for the determination of alcohol have been compared with regard to their accuracy.

2. A method involving oxidation of alcohol with potassium dichromate and sulfuric acid, with subsequent iodimetry, has been tried out and the conditions have been improved upon. Results were accurate to about **0.3%** of the alcohol present.

3. A method for the determination of free alcohol in the presence of ethyl acetate by esterification with acetic anhydride and subsequent decomposition and titration of the excess has been developed. The results are accurate to about 0.2% of the amount of mixture taken.

4. Procedure is given for determining acetic acid with an accuracy of about 0.07% and ethyl acetate to 0.17%.

5. Micro titration of acetic acid in a modified Pilch apparatus has been carried out with 0.01 N solutions and necessary precautions are given. An accuracy of some hundredths or thousandths of the quantity taken was attained.

6. The processes were applied successfully to the analysis of mixtures of all four ingredients.

WARSAW, POLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF CALIFORNIA]

THE CALOMEL AND SILVER CHLORIDE ELECTRODES IN ACID AND NEUTRAL SOLUTIONS. THE ACTIVITY COEFFICIENT OF AQUEOUS HYDROCHLORIC ACID AND THE SINGLE POTENTIAL OF THE DECI-MOLAL CALOMEL ELECTRODE

BY MERLE RANDALL AND LEONA ESTHER YOUNG

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In a careful investigation Gerke[1] found 0.0455 v. for the potential of the cell

$$\text{Ag (elect. crystals)} + \text{HgCl(s)} = \text{AgCl(ppt.)} + \text{Hg(l)} \qquad (1)$$

at 25°, with either molal potassium or hydrogen chlorides as the electrolyte. He also measured the potential of the chlorine electrode against calomel and silver chloride electrodes and found 1.0904 and 1.1362 v., respectively, a difference of 0.0458 v. Gerke used finely divided crystalline silver[2] prepared by rapid electrolysis, and silver and mercurous chlorides "precipitated metathetically in the ordinary granular form from dilute solutions of pure salts."

Brönsted,[3] using a platinum wire plated with silver 0.5 mm. in thickness and with silver chloride after the method of Jahn,[4] obtained 0.0471 and 0.0475 v. at 25° (interpolated) for a cell corresponding to that of Equation 1, with 0.1 N and 0.01 N potassium chloride in gelatin as an electrolyte.

Numerous measurements of the potential of the hydrogen–calomel and hydrogen-silver chloride cells have been reviewed by Lewis and Randall,[5] who found that most of the measurements would fit the same curve if the electromotive force of the cell of Equation 1 was assumed to be 0.0466 v. Later measurements by Harned and Brumbaugh,[6] Harned and Fleysher,[7] Harned and Swindells[8] and by Scatchard,[9] on the hydrogen–silver chloride cell, and by Harned[10] and Randall and Breckenridge[11] on the hydrogen–calomel cell confirmed the value 0.0466 for the difference between these cells.[12]

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

[2] Lewis, *ibid.*. 28, 158 (1906).

[3] Bronsted, *Z. physik. Chem.*, *50*, 481 (1904).

[4] Jahn, *ibid.*, 33, 545 (1900).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York. 1923, pp. 335, 407.

[6] Harned and Brumbaugh, THIS JOURNAL, 44,2729 (1922).

[7] Harned and Fleysher, *ibid.*, 47, 82 (1925).

[8] Harned and Swindells, *ibid.*, 48, 126 (1926).

[9] (a) Scatchard, *ibid.*, 47, 641 (1925); see also (b) *ibid.*, 47,2098 (1925).

[10] Harned, (a) *ibid.*, 42, 1808 (1920); (b) *ibid.*, 48,326 (1926).

[11] Randall and Breckenridge, *ibid.*, 49, 1435 (1927).

[12] This discrepancy was attributed to the silver–silver chloride electrode by (a) Lewis and Randall, ref. 5, and to different forms of silver by (b) Scatchard, THIS JOURNAL, 47, 707 (1925). Gerke's low value (0.0455 v.) was attributed to poisoning of the

Linhart[13] used silver and silver chloride prepared in about the same manner as that used by Gerke.[1] Scatchard[9a] used platinum gauze electrodes plated with silver and then chloridized electrolytically[4,14] in the solution in which they were to be used. Noyes and Ellis[15] used spirals prepared by heating silver oxide[2] supported by a silver plated platinum wire, and then electrolyzed in hydrochloric acid solution. These three forms of silver–silver chloride electrodes appear to agree with other acceptable forms.

The reproducibility of the measurements of the hydrogen–calomel[16] cell is not so great as that of the hydrogen-silver chloride cells. The value 0.3989 v. has been generally accepted as the value of the 0.1 M hydrogen calomel cell at 25°. Yet, notwithstanding the weight of evidence in favor of this value, we shall show that this is too high, and that the true value of the 0.1 M cell is 0.3976 v.

The Reproducibility of Silver–Silver Chloride Electrodes

In the course of these experiments more than 100 electrodes have been used. We shall give only a brief summary of the intercomparisons.

In the first series silver was deposited electrolytically from potassium cyanide solution on platinum foil electrodes about 1 cm. square. These were then covered with a layer of electrolytic silver chloride.[4,17] Three sets of six electrodes each were prepared, but the potentials differed by 0.1–2 mv. Lewis, Brighton and Sebastian[16g] and Güntelberg[18] also prepared and discarded this type of electrode. Horsch[19] prepared several electrodes in this manner, which showed a maximum difference between themselves of 0.9 mv., and which when measured against the hydrogen electrode in 0.01 M acid gave a potential 2.2 mv. higher than our final accepted value. Bronsted's[5] plated electrodes were also high. We may therefore definitely discard the plated platinum foil electrode. It was the experience with these plated electrodes which at the outset led us to ascribe the discrepancies mentioned in the previous section to the silver–silver chloride electrode.

Various forms of silver crystals made by electrolysis have been studied. Large crystals produced by electrolysis with a low current density from silver nitrate solution are far from reproducible. Electrolytic crystals prepared as recommended by Gerke,[1] following the method of Linhart,[13] from a molal solution of silver nitrate, electrolyzed at 90–100° on a point of platinum wire with a current of about 6 amp.. were satisfactory.

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silver-silver chloride electrode by calomel by (c) Nonhebel and Hartley, *Phil. Mag.*, [6] 50, 729 (1925).

[13] Linhart, This Journal, 41, 1175 (1919).

[14] MacInnes and Parker, *ibid.*, 37, 1445 (1915).

[15] Noyes and Ellis, *ibid.*, 39, 2532 (1917).

[16] See (a) Loomis and Acree, *Am. Chem. J.*, *46*, 585 (1912); (b) Tolman and Ferguson, This Journal, 34, 232 (1912), 18° values only; (c) Myers and Acree, *Am. Chem. J.*, 50, 396 (1913); (d) Harned, This Journal, 37, 2460 (1915); (e) Ellis, *ibid.*, 38, 737 (1916); (f) Loomis and Meacham, *ibid.*, 38, 2310 (1916); (g) Lewis, Brighton and Sebastian, *ibid.*, 39, 2245 (1917); (h) Linhart, *ibid.*, 39, 2601 (1917).

[17] Halla, *Z. Elektrochem.*, 17, 179 (1911).

[18] Giintelberg, *Z. physik. Chem.*, 123, 199 (1926).

[19] Horsch, This Journal, 41, 1787 (1919).

More finely divided crystals were made in the same manner from 0.1 *M* silver nitrate solution. The deposit when first formed was a brownish-black sponge, which when touched with a glass rod turned to a grayish-white and dropped to the bottom of the beaker. This form of silver was readily reproduced and electrodes made from it never varied by more than 0.4 mv. when checked against each other or against the best silver–silver chloride spirals.

The spiral oxide-silver, electrolytic silver chloride electrodes (later referred to as silver spirals) were essentially the same as those recommended by Lewis,[2] except that we used a spiral of silver wire, 99.8% pure, instead of a platinum wire spiral plated with silver. A number of the plated platinum spirals were also used, but the greatest difference between the two forms was 0.1 mv. As it shortened the procedure, silver wire was used in later work.

Silver chloride was prepared in the form of "large" granules by metathesis in cold 0.01 M solutions. In the earlier work it was precipitated from silver nitrate solutions with hydrochloric acid after the method of Richards,[20] but it was found more satisfactory and the potentials more reproducible if the precipitation was made from silver perchlorate solutions. In the final experiments the silver chloride was immersed in dilute hydrochloric acid and heated at 90–100° for at least twenty-four hours.

The Potential of Silver–Silver Chloride against Mercury–Calomel

In the preliminary experiments several hundred measurements were made of the various silver–silver chloride electrodes against calomel electrodes prepared as described by Lewis, Brighton and Sebastian.[16g] Mercury and calomel were placed in one side of an H-type cell and silver crystals and precipitated silver chloride in the other. One or two silver spiral electrodes were inserted through well paraffined cork stoppers in each limb of the cell. With 0.01, 0.02, 0.1 and 0.5 M potassium chloride the cells came to equilibrium within an hour.

The difference in potential[21] between the spirals, or between the precipitated silver chloride electrodes with finely divided silver crystals electrolyzed from 0.1 or 1 M silver nitrate solution, or prepared from pure silver oxide by heating, and the calomel was always between 0.0455 and 0.0458 v. In nearly all cases the difference was 0.0455 v. with no measurable difference between the silver–silver chloride electrodes after one hour, and in practically every other case the value approached 0.0455 v. after from fifteen to sixty days. Under the same conditions large electrolytic crystals, prepared at low current densities, gave values between 0.0435 and 0.0445 v. The results are in accord with those of Gerke.[1]

Similar cells, using 0.01, 0.02 and 0.1 M hydrochloric acid instead of potassium chloride, gave erratic results. The potential between the spirals and the calomel gradually increased within a few hours to about 0.0466 v., and after a week to from 0.0469 to 0.0472 v. In acid solution the finely divided silver crystals and precipitated silver chloride usually came to an apparent equilibrium in about twenty-four hours with a potential against the mercury and calomel of 0.0466 v. On standing for several weeks the potential of many of the electrodes decreased, and often reached a value of approximately 0.0455 v. For a time we believed that the difficulty was with the silver–silver chloride electrodes. A glass tube reaching just to the surface of the silver–silver chloride mixture was inserted, and on renewing the electrolyte from a reservoir in the thermostat the value in a few cases decreased several tenths of a millivolt. The same treatment at the calomel electrode caused a similar decrease.

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[20] Richards, THIS JOURNAL, 32, 28 (1910).

[21] The electrical system was the same as that used by Randall and Langford, Tars JOURNAL, 49, 1445 (1927).

The sign of the effect on the renewal of the solution about the calomel electrode indicated that some chloride ions had been removed from the solution in contact with the mercury and calomel.[22] On the other hand, the sign of the effect about the silver–silver chloride electrode indicated that chloride ions were added to the solution, which did not appear to be a plausible explanation. This led us to examine the rate of a possible reaction between hydrochloric acid and mercury.

The Reaction between Dilute Hydrochloric **Acid and** Mercury.—From the potential of the hydrogen–calomel **cell** we may predict that hydrochloric acid and mercury will not react to form calomel and hydrogen at atmospheric pressure unless the molality of the hydrochloric acid is above 11.62 M. However, if oxygen is present mercury will react with dilute hydrochloric acid.

Samples of distilled mercury and 0.01 and 0.1 M hydrochloric acid were sealed in Pyrex flasks and rotated in a thermostat at 25°. After twenty-four hours a slight cloudiness was noted on the surface of the mercury. The reaction then proceeded more rapidly until at the end of four days a voluminous precipitate of calomel was observed. The experiments were repeated, but this time the air was removed from the acid solution by boiling under an atmosphere of hydrogen, in one case, and of nitrogen, in another. The air in the flask was displaced by hydrogen, or nitrogen, before the introduction of the acid. The flasks were then sealed and rotated for seven days without the appearance of any change, and after standing for several months the mercury surfaces were still bright.

Silver–Silver Chloride, Mercury–Calomel and Hydrogen Electrodes

A hydrogen electrode of the form used by Lewis, Brighton and Sebastian[16g] was sealed to the cross piece of the H-cell. No precaution was taken to eliminate air, and the mercury and calomel were shaken or ground in a mortar with the acid in the ordinary manner. The potential of the cell corresponded to a difference of approximately 0.0466 v. between the two chloride electrodes and the potential against the hydrogen electrode was the same as that previously found for each electrode. On standing the difference between the chloride electrodes rose, at times to as high as 0.0480 v. However, on replacing the acid immediately over the mercury by some of the original acid the difference dropped to 0.0455 v. and the potential of the silver–silver chloride hydrogen cell remained constant to 0.0001 v.

Several cells were then set up with calomel which had been rotated, in the absence of air, with mercury and acid which had been boiled in a vacuum. These cells gave the potentials shown in the first four rows of Table I. The first column gives the molality

TABLE I

POTENTIAL OF SILVER–SILVER CHLORIDE, MERCURY–CALOMEL AND HYDROGEN ELECTRODES IN HYDROCHLORIC ACID AT 25°

M	Ag (cryst.) vs. H_2	Spirals vs. H_2	Calomel vs. H_2	Spirals vs. calomel
0.1015	0 3514	0 3514	0 3976	0 0462
.0972	,3536	.3536	.3994	.0458
.0974	.3537	.3539	.3995	.0456
.1233	...	.3422	.3877	.0455
4.095	...	.1194	.1649	,0455
14.84	...	−0.0953	−0.0494	.0459

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[22] (a) Clark, Myers and Acree [J. Phys. *Chem.*, *20*, 264 (1916)] suggest the possibility of oxidation of mercurous to mercuric chloride. (b) See also Gerke, ***Chem.*** *Rev.*, 1, 377 (1925).

of the acid, the second the potential of the finely divided silver crystals and precipitated silver chloride against hydrogen, the third the potential of the spirals against hydrogen, the fourth the potential of mercury-calomel against hydrogen and the last the difference between the spirals and the calomel electrodes.

The Effect of Air in the Acid Calomel Electrode

From the tabulation in a later section it will be found that the results of Table I correspond to a potential of the mercury–calomel hydrogen cell of 0.3977 v. instead of 0.3989 in 0.1 M hydrochloric acid as previously accepted. The following experiments were designed to show that the irregular and high results of previous investigators were due to the presence of air.

An H-cell was set up, mercury–calomel electrodes in each side, and silver–silver chloride spirals in the stoppers over each calomel electrode. To make sure that the materials were properly prepared, the potential in 0.1 M potassium chloride was measured and found to be 0.0455 v. The potassium chloride was now replaced by approximately 0.1 M hydrochloric acid from which the air had been carefully removed. Care was taken to allow no air to enter the cell during the transfer. Temperature equilibrium was established in about fifteen minutes, when the potential was found to be 0.0455 v. between the various spirals and the calomel electrodes. The potential remained constant for five days, when a few bubbles of air were allowed to enter through a glass tube dipping into the calomel. The potential of this electrode rose to 0.0472 against the spirals, but as there was no means of preventing diffusion to the other electrode its potential also rose to about 0.0469 v.

The experiment of the fourth row of Table I was especially designed to test the effect of air. A stopcock was placed in the cross arm of the H-cell. The acid was prepared from constant boiling hydrochloric acid and conductivity water which had been collected in a quartz flask.[23] The air was carefully removed by boiling the solution in a quartz flask with a slow stream of pure nitrogen. Mercury and calomel electrodes were used in place of the silver crystals in the second limb of the H-cell. Both spirals and both calomel electrodes gave the potentials shown in Table I. The stopcock in the cross arm was now closed and a little air introduced at the surface of the mercury. The air was without measurable effect upon the silver-silver chloride spiral, but the potential of the hydrogen-calomel cell with air rose slowly to 0.3882 v. in twenty-four hours and to 0.3894 v. in seven days. The potential of the other calomel electrode remained constant. On replacing the electrolyte over the chloride electrodes with potassium chloride the difference was again 0.0455 v.

It is a remarkable coincidence that so many investigators were able to obtain the same value, 0.3989 v.. at 0.1 M in the presence of air. Harned[10b] obtained 0.3989 v. at 0.1 M but his vacuum technique applied only to the hydrogen electrodes.[24]

Numerous experiments were made with 0.01 M acid which had been freed from air by boiling in Pyrex flasks. The difference between the spirals and mercury–calomel was in every case near 0.0455 v., but owing to the interaction of the glass and dilute acid[23] the values against hydrogen were erratic and were therefore discarded. The difference between the spirals and calomel in 0.01 acid was greater than 0.0466 in the presence of air. Other experiments in more concentrated solutions will be described in a later section.

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[23] See (a) Kraus and Parker, THIS JOURNAL, 44, 2429 (1922); (b) Randall and Scott, *ibid.*, 49, 636 (1927).

[24] Private communication.

After the completion of the foregoing experiments, Güntelberg[18] published his excellent results with the silver–silver chloride electrodes and stressed the necessity of the removal of oxygen. He also suggested that a similar procedure would improve the results with mercury-calomel. Gerke[1] also noted the gradual appearance of alkalinity around calomel electrodes in potassium chloride, which he ascribed to oxygen in the solution.

The effect of mercuric chloride upon the potential of the mercury calomel electrode was studied by Carter, Lea and Robinson,[25] who compared the potential of an electrode of mercury and a solution containing 0.05 N mercuric chloride and 3 N hydrochloric acid with that of an electrode of mercury, calomel and a solution of 3 N acid at 18°. The usual grey film of mercurous chloride appeared on the mercury in the first electrode. The measurements were made against calomel electrodes with potassium chloride solution through a number of liquid junctions the potential of which was probably constant in both cells. The potential of the cell with mercuric chloride showed wide fluctuations (as might be expected) for several days, but tended toward the same potential as that of the calomel electrode. Neither electrode was free from oxygen.

In discussing the relation of our results to those of other investigators, we shall review the thermodynamic properties of hydrochloric acid. Lewis and Randall[5] reviewed the older data and chose 0.2234 v. as the standard potential of the hydrogen–silver-silver chloride cell. Scatchard[9a] recently lowered this value to 0.2226 v. and later,[9b] giving much weight to the theoretical equation of the interionic attraction theory, favored a still lower value, 0.2223 v. We shall find the value 0.2221 v. more consistent with the theory and the experimental results. All available data have been included.

Activity Coefficient from the Freezing Point Measurements

We show in Fig. 1 the values of the freezing point lowering function,[26] $j/m^{1/2}$, for all investigators,[27] plotted against the square root of the molality.

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[25] Carter, Lea and Robinson, *J. Chem. Soc.*, 131, 1906 (1927).

[26] Randall. THIS JOURNAL, 48, 2512 (1926). $j = 1 - \theta/(\nu\lambda m)$, where θ is the freezing point lowering, ν the number of ions formed per molecule of acid, λ is a constant $= 1.858$, and m is the molality.

[27] (a) Barnes, *Trans. Nova Scotian Inst. Sci.*, 10, 129 (1900); (b) *Trans. Roy. Soc. Canada*, [2] 6, 37 (1900); (c) Chambers and Frazer, *Am. Chem. J.*, 23, 512 (1900); (d) Cornec, *Compt. rend.*, 149, 676 (1909); (e) Dernby, Medd. *Vetenskapsakad. Nobelinst.*, 3, No. 18 (1916); (f) Hausrath. *Ann. Physik*, [4] 9, 522 (1902); (g) Jones, *Z. physik. Chem.*, 12, 623 (1893); (h) Jones and Bassett, *Am. Chem. J.*, 34, 290 (1905); (i) Jones and Getman, *Am. Chem. J.*, 27, 433 (1902); *Z. physik. Chem.*, 46, 244 (1903); (j) Jones and Pearce, *Am. Chem. J.*, 38, 623 (1907); (k) Klein and Svanberg, *Medd. Vetenskapsakad. Nobelinst.*, 4, No. 1 (1918); (l) LeBlanc and Noyes, Z. *physik. Chem.*, 6, 385 (1890); (m) Loomis, *Ann. phys. chim.*, [3] 57, 493 (1896); *Phys. Rev.*, [1] 3,

All the values have been converted as far as possible to present atomic weights, and moles per 1000 g. of water in vacuum.[28] For the most part the values of $j/m^{1/2}$ of Hausrath[27f] below 0.002 M are above 0.4. The values of the several series of Randall and Vanselow[27o] are differentiated in the plot. The values of the other investigators cannot be given too much weight. It is noted that the value of $j/m^{1/2}$ tends to decrease rapidly as the molality is decreased below 0.01 M. It was shown by Kraus and Parker[23a] and by Randall and Scott[23b] that the conductance of acid solutions more dilute than 0.01 M decreased with time when measured in glass cells. The effect is larger the more dilute the solution. As the solution remained in the freezing point apparatus longer than the standardizing solution remained in the cell, the tendency would be for the measure&conductance to represent a lower molality than that actually present, and consequently[28b] a smaller j. We have, therefore, drawn the curve to pass to the theoretical limit[26,28] for completely dissociated electrolytes, namely, 0.3'75. The values of $j/m^{1/2}$ in the more concentrated solutions are shown in Fig. 2. The average values of the freezing point calculated from the values of $j/m^{1/2}$, read from the plots of Pigs. 1 and 2, are given in Col. 2 of Table II. Col. 3 gives the logarithm of the activity coefficient at the freezing point, log γ', Col. 4 the logarithm of the activity coefficient at 25°, calculated from the values of log γ'

TABLE II

LOGARITHM OP ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID TO 1 M

m	θ (calcd.)	$-\log \gamma'$	$-\log \gamma_{298}$(F. P.)	$\log \gamma_{298}$	a_1 (298)
0.001	0.003675	0.0150	0 0153	−0.0153	0.999965
002	,007318	.0207	.0211	− .0211	,999928
.005	.018152	0315	,0322	− .0322	.999825
01	036028	.0427	.0438	− .0438	.999650
02	,07143	.0569	,0585	− .0585	.999310
05	,17666	0788	.0812	− .0812	.998295
1	.35209	.0957	0993	− 0993	.99660
.2	.7064	1104	.1155	− 1166	.99321
3	1 0689	.1144	.1210	− ,1213	.98975
.4	1 9-1-03	.1145	.1222	− 1227	.98623
.5	1 8226	.1115	,1203	− .1210	.98262
6	2.2166	.1065	.1162	− .1171	.97891
.7	2.5801	.1002	.1108	− .1118	.97509
.8	2.9050	.0926	.1046	− .1058	.97124
.9	3.2175	.0842	.0972	− .0987	.96726
1 0	3.5172	,0755	.0897	− .0915	.96324

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270 (1896); (n) Nernst, see Roloff, *Z. physik. Chem.*, 18, ***572*** (1895); (o) Randall and Vanselow, THIS JOURNAL, 46,2418 (1924); (p) Roloff, *Z. physik.* Chem., 18,572 (1895); (q) Roth, "Physikalisch-chemische Übungen," 3d ed., L Vosq Leipzig, 1921, p. 58; *(r)* Zecchini, *Z. physik.* Chem., ***19,*** 431 (1896).

[28] See similar discussions, (a) Randall and White, THIS JOURNAL, 48, 2514 (1926), and (b) Randall and Scott, *ibid.*, 49, 647 (1927).

and the preliminary values of the partial molal heat content and of the partial molal heat capacity.[29] Col. 5 gives the final values of log γ taken after a careful study of the electromotive force data. The last column gives the values of the activity of the water at 25°, calculated by means of Equation 8 to be derived later.

Since the foregoing was written and the curves of Figs. 1 and 2 were drawn, we have received the results of a series of freezing point measurements by Chadwell.[30] We have plotted the values of $j/m^{1/2}$ calculated from his freezing points, and find that they are in excellent agreement with the curves as drawn. This confirmation of our interpolation gives us confidence in our method.

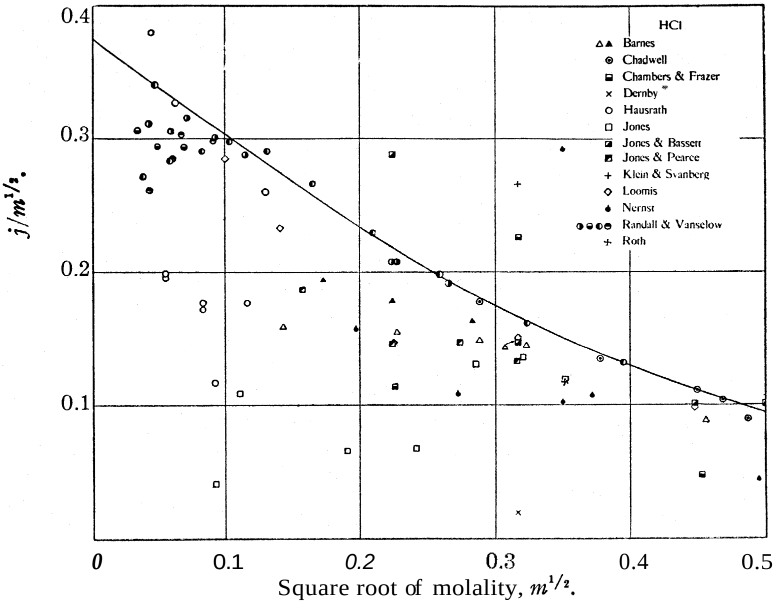

Fig. 1.—Freezing point function for hydrochloric acid.

Calculation of the Activity Coefficient at 25° from the Activity Coefficient at the Freezing Point.—The calculation of the activity coefficient to 25° may be made by three different methods, all of which, theoretically, will give identical results. It may also be made by a fourth method which will give a result differing by a very small amount at 1 M. The first of these methods is that given by Lewis and Randall.[31] The values of their function x plotted against $1/m$ are shown in Curve A of Fig. 3.

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[29] (a) Randall and Rossini (private communication); (b) Randall and Ramage, THIS JOURNAL, 49, 93 (1927).

[30] Chadwell, private communication; see also THIS JOURNAL, 49, 2895 (1927).

[31] Ref. 5, p. 348.

There is some uncertainty in estimating the area under the curve to the limit of very dilute solutions.

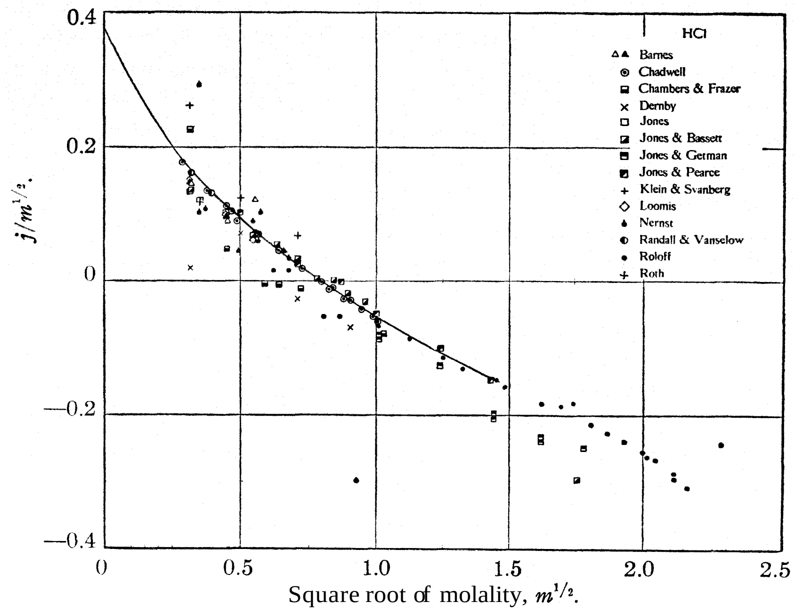

Fig. 2.—Freezing point function for hydrochloric acid.

The same result can be attained if we first calculate in the same manner the activity coefficient at 0° by means of the following equation

$$x' = -\bar{L}_{1_{298}}(y - 0.00006707) + \Delta C_{p_1}(z - 0.00086) \qquad (2)$$

in which $\bar{L}_1$ is the partial molal heat content of the water at 25°, ΔC_{p_1} the increase in partial molal heat capacity at 25° and y and z have the same significance as before, and then change to 25° by means of Equation 5, Appendix III,[5] using the values of $\bar{L}_2$ and ΔC_{p_2}. The values of x' are shown plotted against $1/m$ in Curve B of Fig. 3, from which it will be noted that the uncertainty in estimating the area to the limit of zero concentration is much smaller than in the case of Curve I. The magnitude of the area is also much smaller and the estimation of the area can be made more quickly. (A larger scale plot was used for the estimation.)

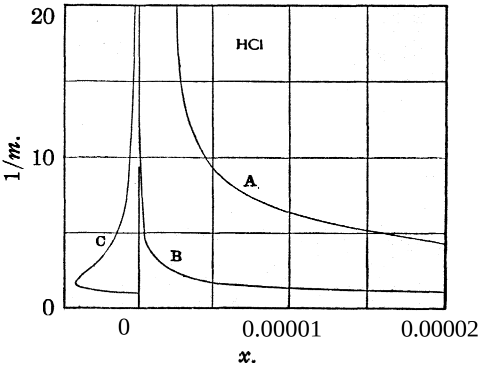

Fig. 3.—x–Function for hydrochloric acid.

The third method was the alternative method of Lewis and Randall in which, for example, the activity coefficient at −3.87°, the freezing point of 1 M acid, was first determined, and the value then calculated to 25°, using the heat content and heat capacity of the solute. The values of x'' are shown in Curve C of Fig. 3. The area is very small [log $(\gamma'/\gamma_{269.23}$ = 0.00051. In employing this method it would be necessary to make a curve for each freezing point, a laborious process. The last calculation, however, illustrates the real significance of log γ', which is nearly but not exactly the activity coefficient at the freezing point, differing for a substance like hydrochloric acid which has a relatively high heat content by only 0.1% at 1 M. The difference at 0.2 M is quite negligible.

We may thus suggest the fourth method which we have used as an approximate method, which assumes that log γ' is actually the activity coefficient at the freezing point and uses the equation

$$\log (\gamma_{298}/\gamma') = -\bar{L}_2 y + \Delta C_{p_2} z \qquad (3)$$

For accurate work in concentrated solutions the second method used is by far the most accurate and convenient.[32]

Activity Coefficient at 25" from Electromotive Force Measurements in Hydrochloric Acid

The reliability of the extrapolation to infinite dilution of the freezing point measurements can be estimated by comparing the activity coefficients found with the results of the electromotive force measurements. For this purpose the quantity, log γ + const., was calculated from the measurements of the various authors[33] by means of the following equation[34]

$$\log \gamma + \text{const.} = -E/(0.00019844 \times 2T) - \log m_{\pm} \qquad (4)$$

in which E is the measured electromotive force and m the molality of the acid. The various values of (log γ + const.) were plotted on transparent paper against the square root of the molality and compared with the curve of log γ, calculated from the freezing points and the temperature coefficient. In this way the best value of the constant was determined to be −1.9964 at 15°,[15] −1.9030 at 18°,[6] −1.9374 at 20°,[18] −1.8778 at 25°,[6,8,9a,13,15,35] −1.8178 at 30°,[6] and −1.7626 at 35°,[15] and −1.8770 for the silver-silver chloride electrode of Harned and Fleysher[7] at 25°. Subtracting these constants at the various temperatures from the calculated values of (log γ + const.) we obtain the values of log y. The difference, *to* 0.2 M, between the values of log γ from the freezing points and that thus calculated from the measurements of the various authors, is shown in Fig. 4.

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[32] The treatment of results of boiling point measurements is entirely similar.

[33] *See* Refs. 6–16, 18.

[34] Randall, *Trans. Faraday Soc.*, *23*, 502 (1927).

The uncertainty in the values of the constants is about 0.0005, corresponding to about 0.1% in the activity coefficient. Comparison shows that the silver-silver chlorides used by the various authors gave like potentials, as was indicated by our experiments in the earlier part of this paper. There the electrolytic silver–precipitated silver chloride electrodes as used by Linhart[13] were found to be slow in coming to equilibrium. His dilute acids were in contact with glass for about a month and it has been shown by Kraus and Parker[23a] that the conductivity of dilute acid solutions decreased rapidly with time. This effect is explained by assuming a disappearance of hydrogen ion, which would give the high values of the e.m.f. observed by Linhart.[13] We thus find $\mathbf{E}^{\circ}_{298} = 0.2221$ v. for the standard potential of the hydrogen silver–silver chloride cell. Scatchard[8] placed great reliance upon the dilute acid measurements of Linhart[13] and used $\mathbf{E}^{\circ}_{298} = 0.2226$ v. This value, however, cannot be consistent with Scatchard's results, the later results of Güntelberg[18] and the freezing point measurements, shown in Fig. 1.

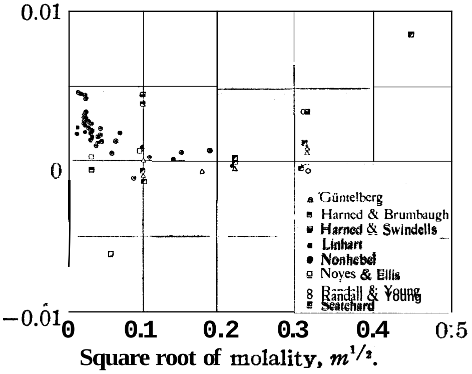

Fig. 4.—Difference between log γ calculated from freezing point and electromotive force data.

The recent careful measurements of Nonhebel[35] with the hydrogen–silver–silver chloride spirals in acid between 0.0001 and 0.05 M are in complete agreement with the measurements of Linhart[13] and confirm the conclusion regarding the identity of electrolytic crystal silver with platinum gauze plated with silver, and of precipitated silver chloride with electrolytic silver chloride. In his experiments he used Jena glass vessels and thus his experiments are open to the same objection as those of Linhart,[13] owing to the reaction of the hydrogen-ion constituent with the glass. Until measurements in the dilute solutions are made using quartz apparatus the question of the correct value of the standard potential and, therefore, of the activity coefficient, will be in doubt. Nonhebel used $\mathbf{E}^{\circ}_{298} = 0.2228$ v., but owing to the known effect of the glass and the agreement of the value $\mathbf{E}^{\circ}_{298} = 0.2221$ with the freezing point measurements of hydrochloric acid and the relation of these measurements to those of other salts, we will choose as the final value, $\mathbf{E}^{\circ}_{298} = 0.2221$ v.

The values of (log γ)/$m^{1/2}$, calculated from the above constants, are plotted" in Fig. 5 against the square root of the molality for solutions above 0.2 M. The activity coefficients from Güntelberg's measurements

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[35] Nonhebel, *Phil. Mag.*, [7] 2, 1085 (1926).

are calculated to 25° by the same values used in transforming the freezing point data. The values of (log γ_{298})/$m^{1/2}$ taken from the freezing point measurements (see Table II) would fall upon the curve within the limits of plotting. A curve corresponding to the curve of Fig. 5 would have fitted the freezing point measurements just as well.

Figure 5 also shows points taken from the various hydrogen–calomel cell measurements. In calculating these points we used the values of the constant, —2.2731 (Ellis[16e]), —2.2757 (Linhart,[16h]) and —2.2722 (Harned,[10b]) (Randall and Breckenridge[11]). The constant for the hydrogen–calomel cell in vacuum would be —2.2624.

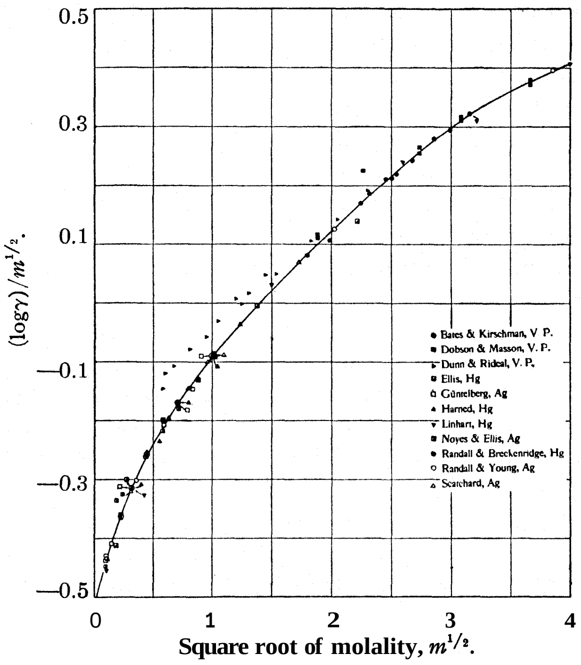

Fig. 5.—Function (logγ)/$m^{1/2}$ for hydrochloric acid.

New Measurements in Concentrated Solutions.—We have obtained two measurements in concentrated solutions (see Table I). Owing to the solubility of the silver chloride in strong acid, the spirals were dipped into the acid for a few minutes during readings after the hydrogen electrode had come to equilibrium. These confirm the difference between the silver-silver chloride and mercury-calomel electrodes in vacuum. When air was admitted to the calomel cells the difference rose to higher non-concordant values. The results of these measurements are also shown in Fig. 5.

Activity Coefficient from Vapor Pressure Measurements

Since the review of the data by Lewis and Randall[6] and Scatchard,[9] several new measurements of the vapor pressure of concentrated solutions have appeared. The values of (log γ + const.) = log $(p^{1/2}/m)$ were plotted[34] against the square root of the molality. By superimposition of the plot upon Fig. 5 we found the constant to be –3.152 at 25°. Fig. 5 shows the values of $(\log \gamma)/m^{1/2}$ obtained in this way.

$$\text{HCl (aq.)} = \text{HCl (g)}; \quad \Delta F^\circ_{298} = 1364.9 \times 2 \times 3.152 = 8604 \text{ cal.} \tag{5}$$

The measurements of Bates and Kirschman[36] at 25° and 30° are the most reliable. The pressures given by Dunn and Rideal[37] at their five lowest molalities when multiplied by a factor of 10 agree with their other measurements. Those of Dobson and Masson[38] are less reliable than those of the former authors. Those of Allan[39] at 18.4° and of Wrewsky, Sawaritsky and Scharloff[40] at 19.95°, 55.2' and 75.9" are in fair agreement with our final curve, while those of Gahl[41] at 25°, of Mitsukuri,[42] and of Yannakis[43] at 50° are erratic. The old measurements of Dolezalek[44] at 30° are in good agreement with the final curve. There appears to be a systematic error in all the measurements, especially below 2 M, where the difficulties of attaining equilibrium are great. (The error is probably caused by entrainment of particles of liquid in the gas stream.)

From the measurements of Dobson and Masson,[38] Dunn and Rideal,[37] Wrewsky, Sawaritsky and Scharloff[40] and Yannakis[43] of the pressure of water over some concentrated solutions, the values of the activity coefficient obtained by the usual methods,[34] are in fair agreement. The interpolated values of the activity of the water of the first two investigations agree with the calculated values in Table III.

Knight and Hinshelwood[45] measured the distribution of hydrochloric acid between benzene and water. Their values of (log γ + const.) = log $(c^{1/2}(\text{benzene})/m)$ were plotted[34] against $m^{1/2}$, but the curve so obtained is much less steep than the curve of log γ against $m^{1/2}$, showing that either the activity of the acid in the benzene phase is not proportional to its concentration or that the experiments are in error.

The final value of the logarithm of the activity coefficient at 25° at

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[36] Bates and Kirschman, THIS JOURNAL, 41, 1991 (1919).

[37] Dunn and Rideal, J. Chem. *Soc.*, 125,676 (1924).

[38] Dobson and Masson, ibid., 125,668 (1924).

[39] Allan, J. *Phys. Chem.*, *2*, 120 (1898).

[40] Wrewsky, Sawaritsky and Scharloff, *Z. physik. Chem.*, 112, 97 (1924); 113, 490 (1924).

[41] Gahl, *ibid.*, 33, 178 (1900).

[42] Mitsukuri, *Sci. Rep. Tohuku Imp. Univ.*, 14, 251 (1925).

[43] Yannakis, *Compt. rend.*, 177, 174 (1923).

[44] Dolezalek, *Z. physik. Chem.*, 26,321 (1898).

[45] Knight and Hinshelwood, J. *Chem. Soc.*, 131,466 (1927).

round molalities, the pressure of the hydrochloric acid and the activity of the water as calculated in the next section are given in Table III.

TABLE III

LOGARITHM OF ACTIVITY COEFFICIENT OP HYDROCHLORIC ACID AT 25° IN CONCENTRATED SOLUTION

m	$\log \gamma$ (298)	p(HCl) atmos.	a_1 (298)	m	$\log \gamma$ (298)	a(HCl) atmos.	a_1 (298)
1.2	−0.0743	5.08×10^{-7}	0.95482	5	0.3757	7.01×10^{-5}	0.73890
1.4	− .0556	7.61×10^{-7}	.94605	6	.5078	1.853×10^{-4}	.67106
1.6	− .0359	1.077×10^{-6}	.93696	7	.6403	4.64×10^{-4}	.6027
1.8	− .0153	1.499×10^{-6}	.92753	8	.7705	1.104×10^{-3}	.5361
2.0	.0080	2.06×10^{-6}	.91750	9	.9000	2.54×10^{-3}	.4720
2.5	.0610	4.11×10^{-6}	.89224	10	1.0189	5.42×10^{-3}	.4146
3.0	.1205	7.78×10^{-6}	.86452	12	1.2367	2.13×10^{-2}	.3162
3.5	.1818	1.405×10^{-5}	.83515	14	1.4368	7.27×10^{-2}	.2371
4	.2460	2.46×10^{-5}	.80401	16	1.6276	0.230	.1740

Activity of the Water[46]

For calculation of the activity of the water we may use the thermodynamic equation,[47]

$$d \log a_1 = -(N_2/N_1) d \log a_2 \tag{6}$$

Substituting for N_2/N_1, $m/55.51$, and for a_2, $a_\pm^\nu$, where $\nu = 2$, the number of ions formed

$$d \log a_1 = -(\nu m\ d \log a_\pm)/55.51 \tag{7}$$

Adding $(\nu m$ d $\log m)/55.51$ to both sides of Equation 7, and writing γ for $a_\pm/m$ we have,

$$d \log a_1 + \frac{\nu m}{55.51} d \log m = -\frac{\nu m}{55.51} d \log \gamma \tag{8}$$

Since, when m = 0, $\log a_1 = 0$, the integration constant is 0, and we can write Equation 8 in the form

$$\log a_1 = -\frac{2m}{55.51 \times 2.303} - \frac{2}{55.51}\int_0^m m\ d \log \gamma \tag{9}$$

The integral may be evaluated graphically by plotting m as ordinate against $\log \gamma$ as abscissa as in Fig. 6, and finding the area under the curve between a given value of $\log \gamma$ and $\log \gamma = 0$. The values of a_1, which we have already given in the fourth column of Table III, were calculated in this manner.

Standard Reference Potentials

Ag(s), AgCl(s), Cl⁻.—Adopting the usual convention that the standard potential of the Pt, H_2(g), H^+ electrode is zero and using our new value of $E°_{298}$ for the hydrogen silver–silver chloride cell, we write

Ag(s), AgCl(s), Cl^-; $E°_{298} = -0.2221$ v.;

$$\text{Ag(s)} + \text{Cl}^- = \text{AgCl(s)} + \text{E}^-;\quad \Delta F°_{298} = 5125 \text{ cal.} \tag{10}$$

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[46] The derivation was made by Randall and Breckenridge but was not published. We have recalculated their work with the later values of the activity coefficient of the acid.

[47] Ref. 5, p. 285.

$Hg(l)$, $HgCl(s)$, Cl^-.—From the value of the hydrogen mercury-calomel cell

$$Hg(l),\ HgCl(s),\ Cl^-;\ E^\circ_{298} = -0.2676\text{ v.};$$

$$Hg(l) + Cl^- = HgCl(s) + E^-;\ \Delta F^\circ_{298} = 6175\text{ cal.} \quad (11)$$

Deci-molal Calomel Electrode.—With mercury and calomel in 0.1 M potassium chloride solution, we may follow Lewis and Randall,[5] and if we assume the activity of the chloride ion to be 0.0772 ± 0.0002 (Randall and White[27a,28a]) we find

$$Hg(l),\ HgCl(s),\ KCl(0.1\ M);\ (D.E.);\ E_{298} = -0.3341\text{ v.} \quad (12)$$

This will be approximately the single potential if we use neutral 0.1 M chloride ion or 0.1 *M* chloride ion in acid in vacuum, but if the measurement is made in acid solution in air, as has been the usual procedure, then the single potential in these cases will be about −0.3354 v.

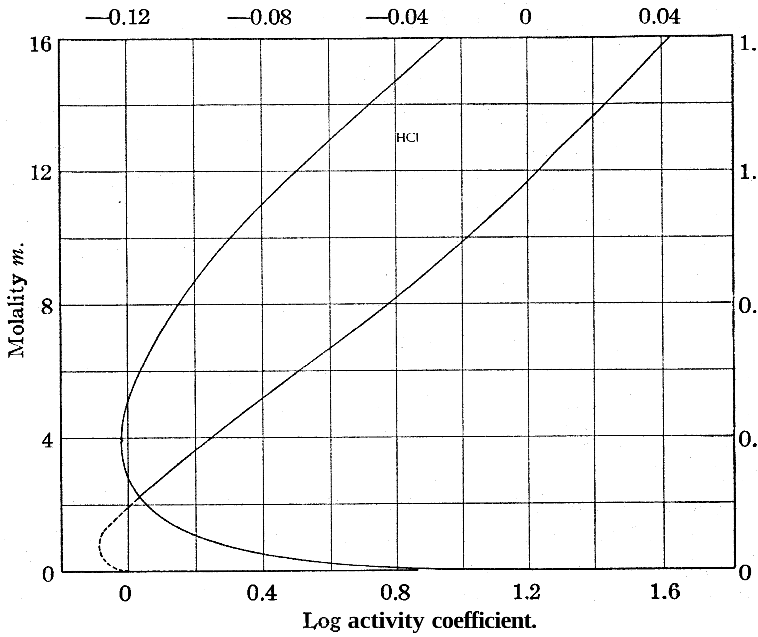

Fig. 6.—Log for hydrochloric acid at 25°. Upper curve shows the dotted portion on *a* larger scale. Use scale at left and at the top.

Normal Calomel Electrode.—The difference between the decimolal and normal calomel electrodes[5] is 0.0529 v. Hence

$$Hg(l),\ HgCl(s),\ KCl(1\text{ mole per liter}),\ KCl(0.1\ M);\ (N.E.);\ E_{298} = -0.2812\text{ v.} \quad (13)$$

These new values will alter most of the values for the single potentials of other electrodes by 0.0010 to 0.0024 v. A general revision of the table of single electrode potentials is in progress.

$Cl_2(g)$, Cl^-, Pt.—Combining Equation 10 with the free energy of formation of silver chloride (—26220 cal., Gerke[1]) we find

$$Cl_2(g), Cl^-, Pt; E^\circ_{298} = 1.3583 \text{ v.}; {}^1/_2Cl_2(g) + E^- = Cl^-; \Delta F^\circ_{298} = -31345 \text{ cal.} \quad (14)$$

Combining with the free energy of formation of mercurous chloride (—25-163 cal., Gerke[1]) we have 1.3581 v. and —31338 cal. The direct measurements of Lewis and Rupert[4*] of the cell Hg(l), HgCl(s), HCl (aq.), $Cl_2(g)$ give $E^\circ = 1.0894$ v. with the acid calomel in air. If we assume the value of the acid calomel electrode in air between 0.2686 and 0.2690 v., we have for the potential of the chloride electrode between 1.3582 and 1.3586 v. in entire agreement with the result from Gerke's measurements.

We also have from Equations 14 and 5

$$ {}^1/_2H_2(g) + {}^1/_2Cl_2(g) = HCl(aq.); \Delta F^\circ_{298} = -31345 \text{ cal.} \quad (15)$$

$$ {}^1/_2H_2(g) + {}^1/_2Cl_2(g) = HCl(g); \Delta F^\circ_{298} = -22741 \text{ cal.} \quad (16)$$

Summary

1. Air causes an error of 0.0010 to 0.0030 v. in the potential of the hydrogen mercury-calomel cell.
2. Dilute hydrochloric acid containing dissolved air reacts with metallic mercury to form calomel.
3. New measurements of the potential of the hydrogen silver–silver chloride cell and of the hydrogen mercury-calomel cell have been made.
4. Air does not seriously affect the potential of the mercury–calomel electrode in neutral chloride solutions.
5. The conditions for the preparation of reproducible silver–silver chloride electrodes have been carefully studied.
6. New values for some important reference electrodes have been calculated.
7. Average values for the freezing point and activity coefficient of the acid, activity of the water and pressure of the acid above solutions of round molalities are given up to 16 M.
8. The free energy of formation of chloride ion and gaseous and aqueous chloride ion has been recalculated.

BERKELEY, CALIFORNIA

[4s] Lewis and Rupert, THIS JOURNAL, 33, 299 (1911); see ref. 5, p. 426.

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 146]

A METHOD FOR ACCURATE DETERMINATION OF THE SPECIFIC HEATS OF SALT SOLUTIONS UP TO 80°; INCLUDING RESULTS FOR POTASSIUM NITRATE AND CHLORIDE SOLUTIONS

BY FRANK T. GUCKER, JR.[1]

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Introduction

The object of this research was to test the interesting theory which F. Zwicky[2] has advanced to account for the abnormally small heat capacity of electrolytic solutions at room temperature. Assuming complete ionization of the salt, he treats by the methods of mathematical physics the several factors influencing the heat capacity of such a solution. By far the most important of these he finds is the attraction exerted upon the rigid electric dipoles of the water molecules in the inhomogeneous field of the ions. This attraction produces a very high pressure in the vicinity of each ion. Since at room temperature increasing pressure decreases the heat capacity of water, that of an electrolytic solution is correspondingly diminished. The same result is not, however, to be expected at all temperatures. Bridgman's[3] work upon the pressure-volume relations of water has shown that with rising temperature the heat capacity of compressed water increases. The change is at first gradual; then much more rapid until, between 60 and 80°, pressure actually increases the heat capacity of water. If Zwicky's theory is correct, at these temperatures the heat capacity of salt solutions should show a corresponding increase.

The few data to be found in the literature are integral values of the heat capacity from high temperature down to that of the room, and are not sufficiently accurate to decide whether or not such an increase generally occurs. The physical conceptions upon which Zwicky's theory is based, if correct, are a very important contribution to our understanding of electrolytic solutions. This research was therefore undertaken to determine accurately the heat capacity of a number of electrolytic solutions over small temperature intervals, up to 80°. The results so far obtained do not suffice to settle the question, but so many experimental difficulties arose and had to be overcome that a description of the final apparatus seems advisable. The work will be continued during the winter, and more complete results will be published shortly.

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[1] National Research Fellow in Chemistry.

[2] Zwicky, *Physik. Z.*, 27, 271 (1926). Summarized in *Physik. Z.*, *26*, 664 (1925) and *Proc. Nat. Acad.*, 12, 86 (1926).

[3] P. Bridgman, *Proc. Amer. Acad. Arts Sci.*, *48*, 310 (1912–13).

Apparatus and Method

The apparatus was a further modification of the "twin calorimeter" method of Joule and Pfaundler, which may be outlined thus.[4] Two similar calorimeters, one containing water and the other the solution under investigation, are placed side by side in a uniform environment. Starting from the same temperature, they are heated by means of two similar electric resistances (one in each calorimeter) connected in series. The difference between the final temperatures of the calorimeters is measured, as well as the total rise in temperature. Knowing the ratio of the resistances, and the weights of water and of solution, the heat capacity of the latter is easily calculated.

For accurate work at high temperatures, where the vapor pressure of water becomes very large and the loss of heat by evaporation correspondingly great, the first requisite was a closed calorimeter system.

At first, Dewar flasks were tried. Into these were ground evacuated glass lids which restricted evaporation to a very small and definite space immediately above the liquid. This arrangement did not, however, prove satisfactory. Too great a heat capacity was evidently involved in the lids, into which the heat penetrated but slowly, requiring at least forty-five minutes to attain thermal equilibrium after an experiment. To remedy this fault, the glass calorimeters were replaced by others made entirely of copper and fitted with copper lids.

Fig. 1 gives an idea of the apparatus as a whole. The two calorimeters CC were suspended within a "submarine" jacket B, immersed in the water-bath A. The calorimeters were fitted with copper lids DD, screwed down upon the gaskets EE (represented by cross-hatching) to give a vapor-tight joint. They were heated by means of two resistance coils (not shown in the drawing);[5] and the difference in temperature between them was measured by the thermel FF. The two thermels GG, connected in series, measured the difference between the mean temperature of the calorimeters and that of the water-bath. The different parts of the apparatus will now be described in more detail.

Environment of Calorimeters.—The adiabatic method had been used previously[4] in order to increase the accuracy of the twin calorimeter apparatus. Each calorimeter was placed in a separate "submarine" jacket, both of which were immersed in a rather large water-bath maintained at the temperature of the calorimeters. In the present research both calorimeters were put inside a single jacket. This made the apparatus much more compact. The resulting reduction in the volume of the water-bath facilitated its temperature control and its stirring and so reduced the chance of error from inhomogeneity in the environment of the calorimeters. Each calorimeter was completely surrounded by a 2-cm. air space, which adequately insulated it from the jacket and the other calorimeter.

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[4] For a description of a somewhat similar apparatus and references to the literature of the subject, the reader is referred to an article by Richards and Gucker, **THIS JOURNAL,** 47, **1876 (1925).**

[5] Shown in detail in Fig. 2. The coils would be directly in front of the stirrers, if shown in Fig. 1.

In addition to the thermal advantage gained by the new arrangement, the calorimeters were placed so much nearer together that the length (and hence the resistance) of the main thermel was greatly reduced and its sensitivity correspondingly increased.

The submarine jacket was constructed in the same manner which had proved satisfactory before[6] from No. 14 B. and S. gage copper, with a lid of the same material clamped down upon a rubber gasket by means of a number of studs and wing nuts.

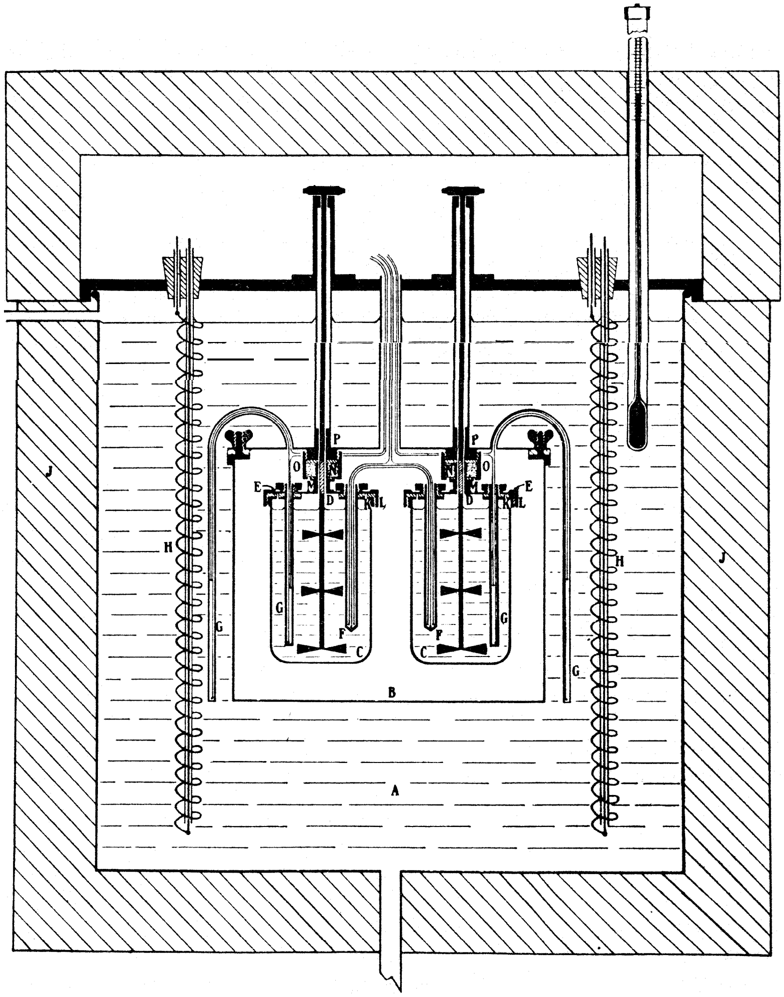

Fig. 1.

The water-bath was heated by four equally spaced coils of bare chromel wire (two of which are shown, HH) connected in series to the lighting circuit. Each coil was wound very loosely around a supporting piece of Pyrex tubing through which one of the heavy copper lead wires was carried. This tube, together with the smaller one used to

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[6] **Ref. 4, p. 1880.**

insulate the upper lead, was held in a two-holed rubber stopper fitting into the brass cover of the water-bath. The water was agitated vigorously by two rotating stirrers (not shown in Fig. 1) each having three propellers mounted on a vertical shaft and run at about 220 r.p.m.

The top layer of an open water-bath, no matter how vigorous the stirring, is always slightly cooler than the rest of the bath, because of evaporation from the surface. In order to prevent this inhomogeneity in the calorimetric environment, a heavy brass lid was fitted completely over the water-bath, leaving an air space of only about 2 cm. above the surface of the water. A two inch layer of plumbers' felt J was fastened around the outside of the container and over the cover on top of the apparatus in order to minimize heat conduction to the room, which otherwise would have caused considerable annoyance and possible errors at the high temperatures.

Calorimeters.—These were spun from No. 14 B. and S. gage copper, with copper lids of the same thickness (1.6 mm.) and were identical throughout. An externally threaded brass ring K was soldered to the top of each, while an internally threaded ring L was soldered to each lid so that it could be screwed down tight upon the calorimeter. A rubber gasket E was used to give a tight joint.[7]

The calorimeters were buffed on the outside and heavily nickel plated and polished. The surface was protected by a thin coating of transparent lacquer which preserved the polish very satisfactorily. The inside of the calorimeter and lid was heavily gold plated but, as usual, this was only partly satisfactory. A gold lining would be preferable and will be used in the later work.

The calorimeters were not supported from beneath in the usual fashion, but were suspended by their lids. This arrangement proved advantageous for its strength and simplicity and for the *ease* with which it allowed the apparatus to be assembled. The calorimeters were held rigidly and perfect alignment of the stirrers was assured.

A small threaded tube M was soldered to the center of each lid, with a hole drilled through it of sufficient size to allow the free passage of the stirrer shaft. On this tube was screwed a small cylinder N of "micarta"[8] held in place by a lock-nut at the top (not shown in the figure). This micarta cylinder in turn was supported by a large nut O threaded to a tube extending up through the top of the submarine jacket and soldered to the latter. The micarta section acted as thermal insulation from the jacket. Thin washers of gasket rubber were put on either side of the micarta to make a vapor-tight joint.[9]

The calorimeters were made with a capacity of about 250 cc. to reduce the quantity of solution required for an experiment. Although this decreased the heat capacity of

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[7] Some difficulty was at first experienced with this gasket, which had a tendency to stick to both calorimeter and lid and twist out of position before the lid was tightly in place. The thread had probably too fine a pitch and a coarse thread would be preferable. Satisfactory results were finally obtained by lubricating the gasket with a small amount of talc, well rubbed in. Other types of gasket (cork and steam packing) were tried, but could not be made air tight.

[8] A material made by impregnating a suitable base with a synthetic resin made by phenol condensation. Hard rubber was first tried but proved unsatisfactory. It softened at 80° and was deformed by the weight of the calorimeter, thus loosening the joint. Not only was the chance of evaporation thus increased, but the stirrer was thrown out of alignment. The micarta proved very satisfactory and showed no tendency to warp even at the highest temperatures.

[9] These washers, of course, did not carry the weight of the calorimeters, as a glance at Fig. 1 will show. When the lid was put in place they were compressed sufficiently so that they did not loosen during an experiment.

the system and so magnified any errors due to thermal leakage, other refinements more than compensated. As good agreement was obtained between experiments as previously, with calorimeters of 600cc. capacity.

Electric Heaters.—The reliability of the method depends upon that of the resistances used to heat the calorimeters, which therefore require careful construction. Satisfactory heaters had been made before[10] from asbestos-insulated constantan wire, threaded through thin brass tubing which was then bent into a convenient shape and gold plated. No asbestos-insulated wire being available for this work, cotton-insulated wire was first tried. The cotton should not have been affected by the temperature to which the resistance wire was heated but, after proving satisfactory for some time, it charred in one place and made the coils unreliable. Several other arrangements were then tried before a successful one was found. It is illustrated in Fig. 2.

The case consisted of a piece of half-inch copper tubing F into the bottom of which a copper disk was silver soldered. The top was threaded internally and fitted with a threaded brass plug *G*, having a hole drilled through the center. The whole case was heavily gold plated on the outside to protect it from the salt solutions.[11]

No. 28 Chromel "A" wire was used for the resistance. This has a low temperature coefficient of resistance change and is unaffected by a current much larger than that used. A piece of the bare wire having a resistance of slightly over 10 ohms was cut and strung with very fine glass beads, which formed a flexible insulation. No. 20 B. and S. copper wires were used as leads. The end of each was drilled centrally to a depth of about 3 mm. The resistance wire was slipped into this hole and silver soldered, making a strong and reliable connection. The resistance of the wire and leads was then measured and the length of the chromel wire adjusted until it was 10.00 ohms (±0.02).

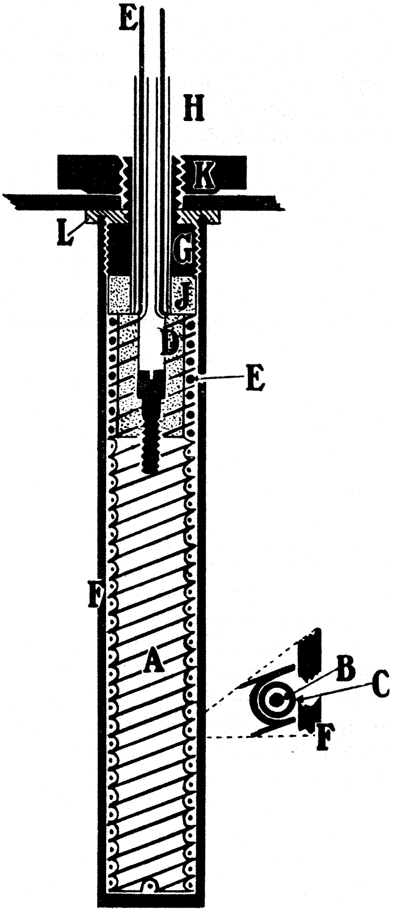

Fig. 2.

A double thread (6 per inch) was now cut in a piece of round copper stock A, Fig. 2. The slot was wide enough to hold the resistance wire B with its beads C and its depth was such that the beads came slightly below the surface of the cylinder. A similar slot was cut across the bottom and the wire was wound bifilar on the copper core. The ends just reached the top, to which was screwed a micarta cylinder D. The micarta carried a square thread (also 6 pitch, double) the width of the copper lead E and deep enough so that the latter, when wound into place, came just below the surface. The lead was

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[10] Ref. 4, p. 1879.

[11] The gold plating has now been replaced by a layer of sheet gold, spun on. This insures protection from any chemical action of the solutions.

painted with several coats of celluloid varnish, which held it in place and provided electrical insulation from the case.[12]

The copper and micarta core was then slipped into the copper case, which it fitted closely. The lead wires were bent toward each other, over the top of the micarta section, and insulated by fine pieces of "spaghetti" tubing H (such as is used in the construction of radio sets). A micarta washer J was put on top, with a hole in the center through which the leads passed. It insulated them from the brass plug G. Its thickness was such that the plug screwed down about 0.5 mm. below the end of the copper tube. The top of the plug fitted through a hole in the lid of the calorimeter where it was firmly held in place by the nut K. A rubber washer L made an air-tight connection. The projecting edge of the copper tube pressed tightly into this and excluded all moisture from the inside of the heater.

Such a heater is rugged and reliable. The case completely protects the wire from the solutions and also from strains which might change its resistance during the course of the experiments. Permanence is essential, since the failure of a heater necessitates not only the construction of a new one, but also the lengthy standardization of the apparatus. The only disadvantage experienced[13] does not seem inherent in the construction of the heater. The use of wire insulated with a thin layer of asbestos, instead of the relatively much thicker glass beads, would probably eliminate most of this lag and will soon be tried.

Thermels **(Thermo-Elements).—These** were all constructed of copper-constantan according to the design of White,[14] and were multiple-junction. The main thermel was made in two opposable sections of 9 junctions each, from No. 34 copper wire and No. 28 "Advance" (constantan), specially tested for homogeneity by White's method. The junctions were distributed over about 3 cm. The total resistance of the thermel was 24.9 ohms. The small thermels were made of finer wire, not specially tested since they were used as a zero instrument. The four junctions of each were spaced far apart, at equal distances, in both calorimeter and water-bath, so as to register the average temperature of each.

Either the main thermel or the two small ones (in series) could be connected to a high sensitivity Leeds and Northrup galvanometer of the all-copper circuit type. This galvanometer was carefully tested and found to have no appreciable zero shift, even after it had been deflected twice as much as in any actual experiment. In reading temperature differences it was therefore reversed by a suitable switch, thus eliminating the effect of any thermo-electric strays in the galvanometer circuit and at the same time doubling its sensitivity. The sensitivity of the main thermel, used in this way, was about 0.0006°/cm. on a scale a little over a meter away from the galvanometer, while that of the two small ones in series was about 0.0012°/cm.

The galvanometer and thermel circuits were protected by a complete equipotential shield and no difficulty was experienced from stray currents.

The thermel cases were metal tubes which reduced the lag in responding to a changing temperature.[15] They were fastened to the calorimeter lids by means of a nut

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[12] This arrangement was, however, designed to minimize the *thermal* insulation. Each lead was held in close proximity to the copper case for 7 cm., so that it might be brought to the temperature of the latter before leaving the calorimeter.

[13] Note 17, p. 1013.

[14] White, THIS JOURNAL, 36, 2292 (1914).

[15] White (ref. 14, p. 2304) found that the substitution of a metal tube for a glass one reduced the lag by about one-half. Dr. L. P. Hall and Dr. B. J. Mair, working in the Gibbs Laboratory, have recently compared a thermel enclosed in a platinum tube with one enclosed in a glass tube and find a ratio somewhat more in favor of the metal case.

threaded to the top of each (see Fig. 1). A shoulder near the top supported a rubber washer which was drawn up against the calorimeter lid to make a tight joint. The thermel wires fitted the tubes rather closely but they were easily removed for inspection and pushed back into the case. The central portion of the wires (above the calorimeter lid) was completely inside the air jacket surrounding the calorimeters and hence required no other enclosure; this was a great improvement over the usual glass or metal case, with its uncertain heat capacity and conductivity to the surroundings.

Calorimeter Stirrers.—These were rotating stirrers with three propellers on each shaft. They were synchronized by a sprocket wheel and chain drive from an induction motor which also drove the stirrers in the outer water-bath. The shafts each ran in two reamed bearings. The upper was just below the sprocket wheel and the lower (P, Fig. 1) just above the submarine jacket, to avoid unnecessary frictional heat in the calorimeter itself. A 2cm. section of bone was threaded in just above the calorimeter lid to prevent thermal conduction along the metal shaft. This section is represented by cross hatching in Fig. 1.

Materials and Solutions.—The potassium nitrate was twice recrystallized and dried as well as possible at 150°. The solution was made up with slightly less than the calculated quantity of water. It was analyzed by evaporating weighed 10cc. samples to dryness in small Erlenmeyer flasks and heating them to constant weight at 200°. A small amount of water was then added to make the solution $KNO_3 \cdot 25.00H_2O$.

The potassium chloride was a good grade of analytical salt. There was not time to recrystallize it, but the small quantities of impurities listed should not have had any appreciable effect upon the heat capacity of the solution. It was fused in small quantities in a platinum crucible to drive off the last traces of water, and the solution was made up to determinate $KCl \cdot 25.00H_2O$.

Method of Standardization.—As before, the apparatus was standardized by means of water, but the procedure was slightly modified. The method was as follows. The same weight of water (W_0) was always put into the left-hand calorimeter (which may be called the "tare"). Enough water (W_1) was then weighed into the other ("working") calorimeter to make the heat capacity of the two systems nearly the same. They were then raised through a 2° temperature interval and the resulting galvanometer deflection was determined. Due correction was made for the slightly different heating effect of the two stirrers, etc., as will presently appear. When a second experiment had been made with the same weight of water in the working calorimeter, a pair of experiments was carried out with a slightly different weight. In this way the galvanometer deflections were determined corresponding to values of W_1 over a 1.5 g. range (the exact balancing weight falling near the center of the range).

A solution was then substituted for the water and the galvanometer deflection corresponding to a certain weight (W_2) was determined. The weight of water (W_1) corresponding to this galvanometer deflection was found by interpolation and the specific heat of the solution obtained by dividing the latter by the former. With this method of standardization neither the heat capacity of the calorimeters nor the sensitivity of the thermel-galvanometer circuit need be determined.

The results of the water standardization are given in Table I.

TABLE I

WATER STANDARDIZATION DATA

	Expt.	Av. temp., °C.	Weight of water (in vacuo), g.	Galvanometer deflection, cm.	Average deflection, cm.
20°	3a	20.04	243.90	+ 5.4	+ 5.4
	4a	19.98	243.90	+ 5.4	
	1a	20.03	244.90	− 4.7	− 4.9
	2a	20.02	244.90	− 5.1	
	5a	20.00	245.40	−10.7	−10.7
	6a	20.04	245.40	−10.7	
50°	3b	50.00	243.90	+ 6.4	+ 6.1
	4b	50.02	243.90	+ 5.8	
	1b	50.00	244.90	− 3.9	− 4.1
	2b	50.00	244.90	− 4.2	
	5b	49.97	245.40	−10.7	−10.8
	6b	50.00	245.40	−10.8	
80°	3c	80.04	243.90	+ 7.9	+ 8.1
	4c	80.02	243.90	+ 8.3	
	1c	79.99	244.90	− 2.0	− 2.2
	2c	80.02	244.90	− 2.4	
	5c	80.02	245.40	− 9.9	−10.1
	6c	80.02	245.40	−10.2	

Experimental Procedure.—To facilitate assembly, the calorimetric apparatus was fastened rigidly to the heavy brass cover of the water-bath which, being counter-weighted, was easily raised or lowered. It carried the heaters and stirrers of the water-bath and also the lid of the submarine jacket; to which in turn were fastened the calorimeter lids, with stirrers, heaters and thermels all in place.

In preparing for an experiment the water and solution were cooled several degrees below the desired temperature, to allow for heat leakage from the room while assembling the apparatus. The calorimeters were then weighed to centigrams and 245.00 g. of water was weighed into the tare which was quickly screwed to its lid. The desired quantity of solution was immediately weighed into the working calorimeter and it was similarly screwed into place. The submarine jacket was then bolted tightly to its lid and the brass cover was lowered, immersing the submarine in the water-bath.

When the motor driving the stirrers was started, the water-bath was brought to the initial temperature of the experiment and the two calorimeters were then raised to the same temperature. In making the final adjustments the current through the calorimeters was cut down by an external resistance and sent through either one, or both, as occasion demanded.

It is impossible to eliminate the heat effect of stirring in the two calorimeters; hence the temperature trend was observed before and after each experiment and a suitable correction applied. With the open calorimeters previously used discrepancies had been observed between the trend before and after an experiment,[16] but with the closed calorimeters a great improvement was noted. In almost every case the two calorimeters tended toward the same temperature.

Ten minutes after the initial temperature adjustments, readings of the galvanometer deflection were made every two minutes, until the temperature trend was uniform for six minutes. Then the experiment was started by passing a current of 0.9 ampere through the heaters; raising the temperature of the calorimeters 2° in about five minutes. The temperature of the water-bath was raised simultaneously and at the same rate, so as to maintain as nearly adiabatic conditions as possible. After the heating current had been turned off, nine or ten minutes were allowed to insure thermal homogeneity in each calorimeter before the galvanometer deflection was read again.[17] The readings were then repeated at two minute intervals for an "after" period of six minutes, to make sure that a steady state had been reached.

During an experiment, the thermels which registered the difference in temperature between calorimeters and water-bath were connected to the galvanometer. By noting the deflection and adjusting the heating currents slightly from time to time, the temperature of the water-bath was kept within about 0.01° of that of the calorimeters (which themselves never differed by more than 0.005°). Somewhat closer agreement was easily maintained during the "fore" and "after" periods, by slightly heating or cooling the water-bath. In this way the heat transfer between the calorimeters and their surroundings was made practically negligible, as is shown by the agreement of the results.

When an experiment was concluded, the apparatus was heated to the temperature desired for the next one. It was thus possible to use the same sample of solution for experiments at 20, 50 and 80°.

A Typical Experiment.—The following is a complete record of a typical experiment, which will illustrate the procedure.

6/24/27	$KNO_3 \cdot 25H_2O$	(Experiment 2a)
Calorimeter + contents	442.14 g.	489.99 g.
Calorimeter	197.14 g.	196.32 g.
Contents	245.00 g. (water)	293.67 g. (solution)

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[16] Ref. 4, p. 1886.

[17] The length of time required was evidently due to the poor heat conduction of the glass beads insulating the heating wires, since equilibrium had been reached much more rapidly when the cotton insulated coils were used. This delay was a disadvantage in that it increased the correction applied for the temperature trend, but fortunately the correction itself was small and no great error was introduced.

Time of reading	Difference	Galvanometer readings Deflection in cm.[a]	Observed change	Time factor[b]
10:13.0	7.0	$1.28	+0.02 (Fore)	1
10:15.0		+1.29		
10:17.0		+1.30		
10:20.0		$1.30		
	14.0		−5.56 (Experiment)	
10:34.0	8.0	−4.26	+0.30 (After)	7/8
10:36.0		−4.16		
10:38.0		−4.08		
10:40.0		−4.04		
10:42.0		−3.96		

Initial temperature 19.00°C.
Final temperature 21.02°C. Av. temp. 20.01°C.

Total rise (AT) 2.02°C.

[a] The deflection caused by reversing the galvanometer

[b] The ratio by which the observed trend must be multiplied to correspond to half the experimental time.

The observed trends, multiplied by the corresponding time factors, become

Trend (fore) = $0.02 cm. Trend (after) = +0.26 cm.
Total trend (corrected to the experimental time) = $0.28 cm.

The corrected change in the galvanometer reading during the course of the experiment was therefore −5.56 − (+0.28) = −5.84 cm. This change was over a range of 2.02'. Corrected to 2.00' it becomes −5.79 cm. The figures are rounded off to the nearest millimeter (corresponding to 0.00006°) AG = −5.8 cm.

By interpolation from Table I, the weight of water which at 20° gives this galvanometer deflection is W_1 = 244.99 g. (in *vacuo*). The weight of solution, corrected to the vacuum standard, is W_2 = 293.90 g., so that the specific heat of the solution is S_{20° = 244.99/293.90 = 0.83358.[18]

The Experimental Results

The specific heats of potassium nitrate and chloride solutions at 20, 50 and 80° are given in the following table.

The accuracy of the method can be gaged by the agreement between duplicate experiments. In the standardization the average difference is

[18] As was pointed out before (ref. 4, p. 1882) the results are subject to a slight correction because the volume of the air space in the calorimeter, above the surface of the liquid, is not the same during the standardization and during an experiment when the thermally equivalent amount of solution is substituted for the water. Also, the vapor pressure from the solution is less than that from the water, so that the heat absorbed by evaporation is slightly different in the two cases. The air space in the calorimeters used in this work was reduced as much as possible and calculations showed that the correction was negligible at room temperature and, although it became noticeable at the higher temperatures, it amounted to only about 0.06% or less.

TABLE II

SUMMARY OF RESULTS

(Specific heat referred to water over the same temperature range)

Expt.	Av. temp., °C.	W_2 (vac.), g.	ΔG, cm.	W_1 (vac.),[a] g.	Specific heat
			KNO_3 $25H_2O$		
1a	20.00	293.90	−5.4	244.95	0.83345
2a	20.01	293 90	−5 8	244.98	,83355
					.83350 (Av.)
1b	50 01	293.90	−8.9	245.31	.83468
2b	50 00	293.90	−9.9	245.38	.83491
					.83480 (Av.)
1c	80 00	293.90	−0.4	244.85	,83311
2c	80.00	293.90	−1.1	244.91	.83332
					.83322 (Av.)
			$KCl.25H_2O$		
1	20.00	293 97	+2.2	244.21	.83073
2	20.01	204.59	−3.3	244.75	.83082
					.83078 (Av.)
3a[h]	49.98	291.96	−0.2	244.57	.8377
3b[h]	80.01	291.96	−1.3	244.96	.8390

[a] Corrected for evaporation.

[b] Unfortunately time did not permit performing a duplicate experiment with the KCl solution at the higher temperatures; but the results listed should be as reliable as any other single experiments.

only 0.1 per mille, and in the experiments 0.2 per mille. The agreement was practically the same at high temperatures as at that of the room, although calorimetric difficulties are greatly increased. Even if the evaporation corrections were considerably in error (which seems most unlikely), the results should be accurate at least to 0.5 per mille.

Discussion of the Results

The results so far obtained certainly show no such increase in the specific heat of the solutions at high temperature as Zwicky's theory would lead us to expect. In the case of the chloride solution, there is a decided increase (1%), but nine-tenths of it occurs between 20 and 50°, which is not to be expected from the prediction of the theory. In the case of the nitrate solution, the specific heat is actually slightly less at 80° than at 20°—a result which is quite surprising since all the solutions previously studied[4] by the writer showed an increase in specific heat of about 2 per mille from 16 to 20°. Evidently a further study of the heat capacity–temperature curves of other salt solutions would be of interest, to see if they are of an entirely different type from that of water.

It may be, as Dr. Zwicky pointed out during a conversation, that not all electrolytic solutions show an increase in heat capacity between 60 and 80°, because in some cases the effect of the pressure caused by the ions is masked by that of hydration, which is doubtless different at different temperatures and cannot be predicted theoretically. A study of a number of different salt solutions should make it possible to settle this question; and this will be undertaken during the next few months.

Summary

An adiabatic twin calorimeter apparatus for the determination of specific heats of aqueous solutions up to 80° has been developed. It is similar in many ways to the apparatus previously used by Richards and Gucker[4] for work at room temperature, but there are many mechanical improvements. The apparatus has been made very compact, allowing the environment to be kept more uniform and the thermel circuit to be made more sensitive. Thermal insulation between the apparatus and the room has been made more effective. The use of closed calorimeters greatly improves the thermometric stability of the system.

The method of standardization has been improved and greatly simplified. It is no longer necessary to determine the sensitivity of the thermel-galvanometer system or the heat capacity of the calorimeters.

The volume of the calorimeters has been reduced from 600 cc. to 250 cc. and the temperature range from 4 to 2°, but other refinements have more than compensated. The accuracy of the method is at least 0.5 per mille, even at the highest temperatures.

The specific heats of solutions of potassium nitrate and chloride have been studied at 20, 50 and 80°. They show no great change over this range. The results so far obtained do not, therefore, confirm F. Zwicky's theory of the specific heat of such solutions. The work is being continued, and more conclusive and detailed results should soon be available.

The writer wishes to thank Professor A. A. Noyes for extending to him the privileges of the Gates Chemical Laboratory and for his generosity in allowing him to take the apparatus East in order to complete the research. He also wishes to thank Mr. E. H. Searle for many mechanical suggestions and for his help in constructing the apparatus.

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NOTE ON THE J. LAWRENCE SMITH METHOD FOR THE ANALYSIS OF SAMARSKITE[1]

BY ROGER C. WELLS

RECEIVED NOVEMBER 21, 1927 PUBLISHED APRIL 5, 1928

The mineral samarskite and several closely related species have long been known to offer analytical problems quite different from those met in the analysis of silicates. These minerals contain columbium, tantalum, the rare earths, uranium, and a considerable number of the more common elements, such as iron, manganese, calcium, lead, zinc and titanium.

The principal methods that have been proposed for the decomposition of such minerals are: (1) heating with sulfuric acid;[2] (2) fusion with potassium or sodium hydrogen sulfate;[3] (3) treatment with hydrofluoric acid;[4] (4) heating in the vapor of sulfur monochloride.[5]

The method of J. Lawrence Smith, involving the use of hydrofluoric acid, has considerable historical interest and still presents important analytical problems. It has the advantage of accomplishing a rapid decomposition of the mineral without introducing any alkali salts. Silica, if present, must be estimated separately, but it is seldom found in samarskite itself.

Outline of the Method

A brief outline of Smith's method may assist the reader. He used 5 g. portions but with present-day facilities 2 g. portions are probably sufficient.

The finely powdered mineral is weighed, placed in a platinum dish, covered with hydrofluoric acid and allowed to stand or heated on the steam-bath until decomposition is complete, as evidenced by the disappearance of all dark specks. Decomposition is assisted by stirring with a platinum rod. After standing overnight, cold, the insoluble portion, **A,** is filtered on a paper supported by a platinum cone or rubber funnel, well washed with dilute hydrofluoric acid, finally transferred to a platinum dish and heated with a moderate excess of sulfuric acid until nearly all of the sulfuric acid is evaporated. Taken up in water, this portion is supposed to contain the rare earths and uranium.

The filtrate, B, soluble in hydrofluoric acid is also evaporated with an excess of sulfuric acid and finally taken up in water with a little hydrochloric acid. On diluting and boiling, if not before, this solution deposits columbium and tantalum oxides. Titanium, tin and tungsten are sup-

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[1] Published with the permission of the Director of the U. S. Geological Survey.

[2] Hoffman, Am. *Jour. Sci.,* [3] 24,475 (1882).

[3] Nilson, Ber., 13, 1430 (1880).

[4] Smith, Am. *J. Sci.,* [3] 13, 359 (1877); and especially Am. Chem. J., 5, 44, 73 (1883).

[5] Hicks, THIS JOURNAL, 33, 1492 (1911).

posed to accompany the columbium. The filtrate from the "acid earths" carries iron, manganese and most of the other bases that may be present.

Several helpful comments on this method of analyzing samarskite have been made by Hillebrand[6] whose paper should be consulted for some alternative procedures and additions.

The scheme of analysis finally adopted and discussed in this paper is shown in the accompanying diagrammatic form.

SCHEME FOR THE ANALYSIS OF SAMARSKITE

<table>
<tr><td colspan="7">Moisten 2 g. of the finely powdered mineral, add HF, stir or heat until decomposition is complete.</td></tr>
<tr><td colspan="4">A. Insoluble: Rare Earths, Pb, U, (Fe, Mn), Ca, etc. Fume with H_2SO_4. Saturate with H_2S.</td><td colspan="3">B. Soluble: Cb, Ta, Ti and most of the bases. Fume with H_2SO_4. Evaporate. Take up in a little HCl and considerable SO_2. Boil.</td></tr>
<tr><td rowspan="4">Precipitate: PbS and insoluble.</td><td colspan="3">Filtrate: Boil. Acidify with HNO_3. Boil. Add NH_4Cl and NH_4OH.</td><td rowspan="2">Precipitate: Cb, Ta, Ti (Sn, W). Weigh. Dissolve in $NaHSO_4$. Pass a portion through a reductor and titrate the Cb.</td><td colspan="2">Filtrate: Oxidize iron, add NH_4Cl and NH_4OH. Filter.</td></tr>
<tr><td colspan="2">Precipitate: Dissolve in HNO_3. Evaporate and pour solution into $H_2C_2O_4$</td><td rowspan="2">Filtrate. Combine with similar filtrate in B portion.</td><td rowspan="2">Precipitate: Dissolve. Treat with $(NH_4)_2CO_3$ Filter. Add filtrate to that from FeS in A.</td><td rowspan="3">Filtrate: Determine Mn, Zn, Ca, Mg, K and Na in usual way.</td></tr>
<tr><td rowspan="2">Precipitate: Th and Rare Earths,</td><td>Filtrate Add $(NH_4)_2CO_3$. Remove Fe, etc., with $(NH_4)_2S$.</td><td></td></tr>
<tr><td colspan="4">Solution: U. Evaporate, ignite, dissolve in HNO_3, filter, precipitate with NH_4OH, filter, ignite.</td></tr>
</table>

Observations and Suggestions

Experience with this method has shown that it is not as simple or clean-cut in its separations as the original description might lead one to suppose. Some suggestions and additions are given in the following paragraphs, relating chiefly to work done on a specimen of samarskite collected from a pegmatite about two and a half miles southwest of Petaca, New Mexico, by Mr. F. L. Hess, of the Bureau of Mines, U. S. Department of Commerce. The results given here refer only to an average lot of certain picked portions that was first analyzed. Later tests showed that the mineral was not of uniform composition throughout. The genetic relations of the different portions and the geological features will be considered elsewhere.

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[6] Hillebrand, *Col. Sci. Soc. Proc.*, 3, 38 (1888).

1. The paper on which the fluorides are filtered should be carefully treated for a small quantity of earths invariably retained by it, by gently igniting and adding the residue to the main **A** portion before all the sulfuric acid is evaporated.

2. Practically all of the lead, which is of interest now-a-days on account of its supposed genetic relation to uranium and thorium—their ratio permitting a determination of the "age of the mineral"—may be filtered off from the solution of the rare earth sulfates as $PbSO_4$. If small in amount, it is separated as PbS and eventually determined by the Fairhall method,[7] which consists in separating the lead as $PbCrO_4$, and titrating the chromate iodimetrically with thiosulfate; or the lead may be weighed as $PbCrO_4$. It is of historical interest to note that Smith supposed the insoluble in sulfuric acid to be Cb_2O_5 and added its weight to the main Cb_2O_5. On the other hand, Hillebrand considered it to be all $PbSO_4$, which it is not always. **A** small fraction of the lead may escape determination as $PbSO_4$, but only a trace will be found in the B portion when hydrofluoric acid alone is used to decompose the mineral.

3. On account of the almost certain contamination of the rare earth oxalates by calcium, manganese, zinc and sometimes uranium, if they are precipitated with oxalic acid immediately after removing lead, it is advisable to make two or more precipitations first with sufficient ammonia and ammonium chloride, dissolve the hydroxides in nitric acid, evaporate the excess and then precipitate the rare earths as oxalates.

4. It is unnecessary to describe the determination of manganese, zinc, calcium, magnesium and the alkalies here except to say that it is advisable to evaporate the main filtrate somewhat to recover any uranium that may have been washed through the filter in the absence of an electrolyte in the wash water.

5. In regard to the precipitation with oxalic acid the fear expressed by Hauser[8] that uranium and iron may carry considerable rare earths into the filtrate was found to be groundless when dilutions appropriate to analytical work were used. Thorium is separated from the other rare earths by the well-known thiosulfate method. The remaining earths are separated by means of several treatments with sodium sulfate into two groups, the insoluble cerium-terbium group and the soluble yttrium group Cerium is determined by oxidation in sulfuric acid solution with ammonium persulfate and titration with hydrogen peroxide.[9] **A** very little, apparently, remains in the "yttrium group."

6. Iron is separated from uranium in the **A** portion by means of ammonium carbonate (about *2* g. to 15 ml. of ammonia) and ammonium sulfide (considerably more than the "few drops" recommended in some books, to avoid colloidal effects). The uranium solution is evaporated and the residue ignited. After dissolving in nitric acid and filtering off the residue of platinum, etc.—probably all derived from utensils and reagents—the operation is repeated. Blank tests showed that beryllium remains with the uranium in this treatment, if present. Uranium is then precipitated by ammonia and weighed as U_3O_8. The weight so obtained was very close to that obtained by titration with permanganate. The uranium solution cannot be ignited directly to U_3O_8 on account of the presence of sulfates, as uranyl sulfate does not go to U_3O_8 on ignition.

As noted by Hillebrand, the uranium is not all found in the **A** portion, but it seems doubtful whether the distribution between the **A** and B portions gives the UO_2 and UO_3 of the mineral exactly. Several factors, such as the insolubility of uranous fluoride, the ionization of ferric fluoride and the proportion of femc iron present, come

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[7] Fairhall, *J.* Ind. *Hygiene,* 4,9 (1922); also Kehoe and others, **J.** ***Am.*** Med. ***Assocn.,*** 87,2081 (1926).

[8] Hauser, *Z. anal. Chem.,* 47, 677 (1908).

[9] Schoeller and Powell, "The Analysis of Minerals and Ores of the Rarer Elements," Griffin and Co., London, 1918, p. 73.

into play here. A consideration of these factors makes it appear advisable to express the reducing power of the mineral, as determined by solution in sulfuric acid in a sealed tube and titration with permanganate, first as UO_2 and any remaining as FeO.[10]

7. The small precipitate of iron in the A portion is tested for SiO_2, Mn, Zn, Ti, Al, Cb and other elements. Aluminum could not be found in samarskite and SiO_2 was very doubtful.

8. The sulfates obtained from the B portion are evaporated short of dryness, moistened with about 2 ml. of hydrochloric acid and about 10 ml. of saturated SO_2 solution, diluted to about 400 ml. and boiled to hydrolyze the acid earths. This process is repeated until the earths are free from iron and their recovery from the filtrate is as complete as possible. They are then weighed as $Cb_2O_5 + Ta_2O_5 + TiO_2$. The titanium is then determined colorimetrically, and Ti + Cb volumetrically by means of a Jones reductor and titration with $KMnO_4$.[11] This method even if somewhat approximate is far preferable to the method of Marignac. Sears' method[12] proved unreliable as a quantitative method.

9. The filtrate from the hydrolysis of the acid earths is analyzed as has been described for the A portion, except that iron is separated by ammonium carbonate without the use of ammonium sulfide, bringing the solution just to boiling. When the distribution of the elements between the A and B portions is of no consequence the uranium portions, the iron portions and the manganese portions can be combined with a great saving of time.

TABLE I

ANALYSIS OF SAMARSKITE FROM PETACA, NEW MEXICO

	Insoluble in HF	Soluble in HF	Total		Insoluble in HF	Soluble in HF	Total
Cb_2O_5	..	41.00	41.00	MnO	0.20	0.47	0.67
Ta_2O_5	..	4.62	4.62	ZnO	.06	.03	.09
TiO_2	..	2.20	2.20	Ba, Sr	..	..	Traces
SnO_2	..	.04	.04	CaO	2.57	.05	2.62
WO_3	..	.02	.02	MgO	.13	.04	.17
UO_2	5.83	..	6.14[a]	PbO	.84	.02	.86
UO_3	..	2.41	2.08[a]	K_2O	.10	.11	.21
Ce_2O_3	.20	..	.20	Na_2O	.04	.06	.10
$(La, Tb)_2O_3$, etc.	4.56	..	4.56	H_2O	..	1.31	1.31
Y_2O_3, etc.	27.54	..	27.54	Undetermined	.30	.25	.55
ThO_2	1.55	..	1.55	He	..	..	Present
ZrO_2	..	.02	.02				———
Fe_2O_3	.71	2.33	3.04	Total, per cent.			99.69

[a] Stage of oxidation based on titration with $KMnO_4$.

Physical and Optical Data

Determination of the density of some mineral fragments in the pycnometer at 25° gave 5.670. Another lot of fragments of somewhat different

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[10] There is scarcely any reason why we should not write Mn_2O_3 and CeO_2 but it is not conventional in these minerals.

[11] One mg. TiO_2 = 0.1247 ml. of 0.1 N $KMnO_4$. My latest experience is that 1 ml. of 0.1 *N* $KMnO_4$ = about 7.55 mg. Cb_2O_5, although Metzger and Taylor found 7.052 mg. Cb_2O_5 [*Columbia School of Mines Quart.*, 30, 323 (1909)]. Further details are given in a dissertation by David Hart, Columbia Univ., 1926.

[12] Sears, THIS JOURNAL, 48, 343 (1926).

composition gave 5.656. The hardness and other physical properties of the mineral agree with Dana's description of samarskite. Its index of refraction, determined by Dr. C. S. Ross, of the U. S. Geological Survey, is somewhat variable between 2.18 and 2.20. It is isotropic. Unfortunately the pieces of mineral give no indication of external crystal form. The rock surrounding them is stained somewhat brown. After the above analytical work was completed radiographs of polished sections of the mineral and rock showed some unhomogeneities and zoning and further analyses of certain portions will probably assist in making the geologic relations clear, but this work may not be completed for some time and will be published elsewhere.

Test for Helium

Helium was identified spectroscopically by the method used for brannerite[13] in 1920. In fact, by means of a direct-reading Hilger spectroscope, the spectrum tube used in 1920 was reëxamined more carefully and compared with one containing gas from samarskite, with the results shown below. There is no doubt that the yellow line 5876 is slightly removed from the two sodium lines, and several other helium lines were observed. Some lines, however, are still not classified with certainty.

TABLE II

DATA ON HELIUM LINES

Gas from brannerite observed in 1920	Observed more accurately in 1927	Gas from samarskite observed in 1927	Gas from brannerite observed in 1920	Observed more accurately in 1927	Gas from samarskite observed in 1927
	He lines			Other lines	
6660		6698 (N_2?)	7000	6081 very faint	
5880	5875	5876		6067 very faint	
5030	5013	5014	6070	6020 very faint	
		4923		5981 very faint	
4720		4715		5972 very faint	
4470		4472		5938 very faint	
	H_2 lines		5620	5931	
6545	6569	6569		5812	
4870	4863	4863	5470	5610 green band	5609
					5462
			5200	5198 green band	5199
					5044

Age of the Mineral

The approximate age of the material analyzed, based on Pb = 0.80, U = 7.14, and Th = 1.36, computed by the equation

$$\text{Age} = \frac{\text{Pb}}{\text{U} + 0.38\,\text{Th}} \times 7900 \text{ million years}$$

gives 1040 million years, but this is only an average, as the mineral is not homogeneous and it is accordingly difficult to evaluate what weight

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[13] Hess and Wells, *J. Franklin Inst.*, 189,225 (1920).

should be attached to this figure. It is hoped, however, that the preparation of radiographs may assist in indicating the less altered portions of the material and, if so, an age determination of the unaltered portion may have greater significance.

Summary

A study of the J. Lawrence Smith method of analyzing samarskite has been made, showing how the different elements distribute themselves in the treatment with hydrofluoric acid. Precautions to be observed in completing the different determinations are given.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH]

THE HYDROLYSIS OF SUCROSE BY HYDROCHLORIC ACID IN THE PRESENCE OF ALKALI AND ALKALINE EARTH CHLORIDES[1]

BY C. F. KAUTZ AND A. L. ROBINSON

RECEIVED DECEMBER 7, 1927 PUBLISHED APRIL 5, 1928

The Influence of Neutral Salts on the Acid Inversion of Sucrose

Introduction

It has long been known that neutral salts exert an accelerating influence on reactions of substances subject to catalytic decomposition in acid solutions. Since the original discovery of this phenomenon in the case of sugar hydrolysis by Lowenthal and Lenssen,[2] a large amount of work has been done and a rather extensive literature has resulted. A summary of the earlier work, especially that concerning sugar hydrolysis, is given by Caldwell.[3] A discussion of later work, giving an account of some of the theories which have been proposed to explain this phenomenon, will be found in a recent paper by Bowe.[4] An excellent review of the present status of the problem is given by Schmid and Olsen.[5]

In recent years there have been many attempts made to explain the phenomenon in terms of the activity of the hydrogen ion in the reacting mixture, and the present view of several recent investigators is that the rate of decomposition of a compound by hydrogen or hydroxyl ion catalysis in salt solutions is related to the activity coefficients of these ions. Quali-

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[1] This paper is an abstract of the thesis submitted by C. F. Kautz to the Graduate School of the University of Pittsburgh in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Lowenthal and Lenssen, *J. prakt. Chem.*, 85, 321 (1862).

[3] Caldwell, *Report Brit. Assoc. Adv. Sci.*, 1906, p. 267.

[4] Bowe, *J. Phys. Chem.*, 31, 297 (1927).

[5] Schmid and Olsen, *Z. physik. Chem.*, 124, 97 (1926).

tatively, Åkerlöf[6] states that increase of the activity coefficient increases the velocity, and decrease of the activity coefficient decreases the velocity of the reaction in the case of hydrogen ion catalysis. References to a number of recent investigations illustrating this viewpoint are given by Åkerlöf in the article just quoted.

This investigation is an attempt to compare the rate of inversion of sucrose, using hydrochloric acid as the catalyst, in the presence of several univalent and bivalent chlorides, with the activity coefficients of the hydrogen ion in hydrochloric acid solutions containing the same salts. The activity coefficient data available in the literature are, however, for solutions not containing sucrose.

An empirical relation between the molar concentration of salt and velocity constant, proposed by Schmid and Olsen[6] as being of general application in describing the action of neutral salts in affecting hydrolytic reactions, has been tested with regard to its applicability to the inversion of sucrose. According to these investigators, the neutral salt action is described by the relation $K = K_0 \times 10^{rC}$, where K_0 is the velocity constant in the absence of salt, C is the concentration of added salt in moles per liter and r is an arbitrary constant.

Experimental Part

Materials.—The sucrose used in this work was of a pure commercial grade of cane sugar. It contained 0.05% of moisture and 0.005% of ash. It polarized 99.9° Ventzke at 20° and was considered to be of a sufficient purity for use in this work. It was kept in a desiccator over concentrated sulfuric acid.

Potassium, sodium, lithium, barium, calcium and strontium chlorides were used. The commercial C. P. grade was used and, with the exception of the lithium and calcium chlorides, they were purified by recrystallization three times from distilled water and were dried in an electric oven at 105–110°. The barium and strontium chlorides were dried at 120°, as at that temperature they lose completely their water of crystallization. The lithium and calcium chlorides were used in the form of concentrated solutions, which were standardized by determining chlorine as silver chloride.

Standard hydrochloric acid was prepared from constant boiling hydrochloric acid made according to the method of Foulk and Hollingsworth.[7]

Apparatus.—The saccharimeter used in this work was a Schmidt and Haensch triple field, Soliel-Ventzke type instrument.

The polarimeter tubes were 200 mm. long and were provided with metal jackets through which water was circulated from a thermostat. The tubes were provided with tubulures for thermometers.

The thermometers used were compared with a standard thermometer and corrections applied.

A 75-watt, 110-volt "Mazda" lamp was taken as the light source, the light being filtered through a 3 mc. layer of a 3% potassium bichromate solution.

Experimental Procedure.—The experiments were carried out in all cases using 20 g. of sugar to 100 cc. of solution For each determination 50 g. of sugar and a quantity of

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[6] Åkerlöf, This Journal, 48, 3046 (1926).

[7] Foulk and Hollingsworth, *ibid.*, 45, 1220 (1923).

the desired salt which when dissolved and diluted to 250 cc. would give the desired concentration, were accurately weighed and introduced into a calibrated 250cc. volumetric flask. In the case of the lithium and calcium chlorides the required amounts of the standardized solutions were added by means of a calibrated buret.

The sugar and salt were then dissolved in distilled water at 25.0°, allowing space for the addition of the hydrochloric acid. A quantity of standardized acid, also at 25.0°, was then added from a calibrated buret, such a quantity being taken that when filled to the mark the acid concentration was 0.100 *N*.

The solutions were thoroughly mixed and transferred to the polarimeter tubes and readings taken at different time intervals, the temperature being maintained at 25.0 ± 0.05°. All readings were corrected for the "zero" reading of the instrument, which was frequently determined during the course of an experiment.

The flask containing the solution remaining after filling the polarimeter tubes was immersed in a thermostat at 25 ± 0.05°, for use in determining the final rotation. This final reading was taken at least forty-eight hours from the start of the reaction.

Method of Calculating Results.—The reaction velocity constants are calculated according to the ordinary monomolecular formula

$$K = \frac{1}{t} \log,, \frac{r_0 - r_\infty}{r - r_\infty}$$

where r_0 is the rotation at zero time, r is the rotation at a time t and r_∞ is the final rotation. Because of the experimental difficulties involved in directly determining initial rotations, and also because of the decrease in rotation of sucrose due to the presence of the salts, r_0 was indirectly determined using the method of Rosanoff, Clark and Sibley[8] and applying the method of least squares.

Results and Discussion

The results obtained in this investigation are given in Table I. The first column gives the molar concentration (moles per liter) of the salt, the second gives the experimentally determined velocity constant K, the third gives the ratio of the velocity constant to that obtained in the absence of salt and the fourth gives the $\log_{10} (K \times 10^4)$.

TABLE I

VELOCITY CONSTANTS FOR THE INVERSION OF SUCROSE WITH 0.100 *N* HYDROCHLORIC ACID IN THE PRESENCE OF NEUTRAL SALTS

Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\log_{10} (K \times 10^4)$	Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\log_{10} (K \times 10^4)$
0.000	0.430	1.00	0.6338				
	Potassium Chloride				Barium Chloride		
.050	.452	1.05	.6551	0.050	0.452	1.05	.6551
.100	.460	1.07	.6628	.100	.461	1.07	.6637
.200	.493	1.15	.6929	.200	.489	1.14	.6893
.500	.543	1.26	.7348	.500	.588	1.37	.7694
1.000	.648	1.51	.8116	1.000	.817	1.90	.9122
2.000	.962	2.24	.9832	1.300	.968	2.25	.9859
3.000	1.343	3.12	1.1281				

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[8] Rosanoff, Clark and Sibley, THIS JOURNAL, 33, 1911 (1911).

TABLE I *(Concluded)*

Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\log_{10} (K \times 10^4)$	Concn. of salt, moles/liter	$K \times 10^3$	K/K_0	$\log_{10} (K \times 10^4)$
	Sodium Chloride				Strontium Chloride		
0.050	0.472	1.10	.6739	.0050	0.600	1.16	.6990
.100	.485	1.13	.6857	.100	.533	1.24	.7267
.200	.506	1.18	.7042	.200	.568	1.32	.7544
.500	.547	1.27	.7380	.500	.649	1.51	.8122
1.000	.661	1.54	.8202	1.000	.959	2.23	.9818
2.000	.972	2.26	.9877	1.300	1.217	2.83	1.0853
3.000	1.492	3.47	1.1738				
	Lithium Chloride				Calcium Chloride		
0.050	0.460	1.07	.6628	.050	0.448	1.04	.6513
.100	.491	1.14	.6911	.100	.476	1.10	.6776
.200	.522	1.21	.7177	.200	.517	1.20	.7135
.500	.561	1.30	.7490	.500	.635	1.48	.8028
1.000	.676	1.57	.8300	1.000	.942	2.19	.9741
2.000	1.082	2.52	1.0342	1.300	1.188	2.76	1.0748
3.000	1.746	4.07	1.2420				

In each determination at least twelve readings were taken, at time intervals ranging from thirty minutes to two hours, the result given in the table being the average of these constants. In all the runs the average deviation from the mean was not more than 1%.

For comparison with the activity coefficients of the hydrogen ion in 0.100 N hydrochloric acid, containing similar amounts of these salts, use was made of the data of Harned[9] and Harned and Brumbaugh,[10] who have calculated, from electromotive force measurements, the activity coefficients for the hydrogen ion in 0.100 N hydrochloric acid containing various amounts of the chlorides of the metals used in this investigation. In order to obtain the activity coefficient and velocity constant data for comparable concentrations, it was necessary to convert the molal concentrations used by Harned to the molar basis. For the alkali chlorides Harned gives the concentrations expressed in both systems. In the case of the alkaline earth chlorides this conversion was effected by accurately making up from these salts a series of solutions in 0.100 N hydrochloric acid and determining their densities at 25.0° using a pycnometer.

In order to effect a comparison between the observed velocity constants and the activity coefficients of the hydrogen ion, the data are plotted as shown in Figs. 1 and 2. The abscissas, representing velocity constant and activity coefficient of the hydrogen ion, have been so chosen that starting the two sets of curves at a common point, the units selected represent equal percentage increases in the variables. The velocity

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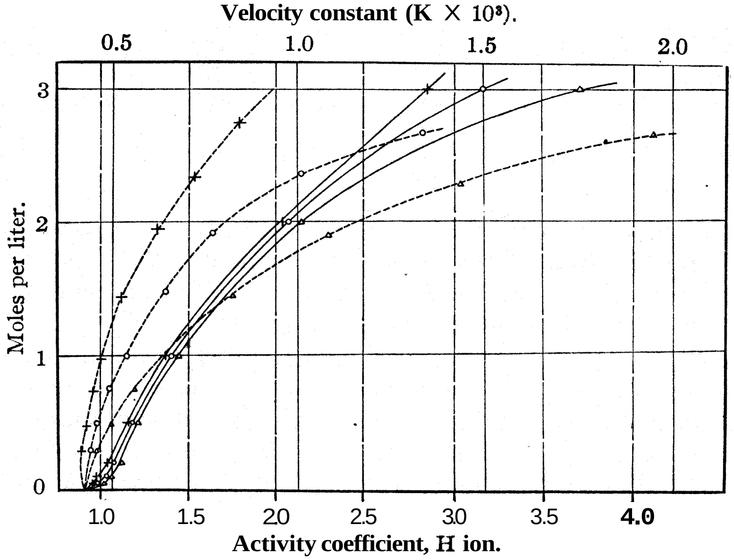
[9] Harned, THIS JOURNAL, 42, 1808 (1920).

[10] Harned and Brumbaugh, *ibid.*, 44, 2729 (1922).

constant curves are shown as solid lines and Harned's data, with concentrations expressed on the molar basis, are shown as broken lines.

Inspection of the curves indicates that there is no simple relationship between activity of the hydrogen ion, as determined in solutions containing no sucrose, and rate of hydrolysis. In the case of the alkali chlorides the curves are in the same order, but in the case of the alkaline earth chlorides, strontium chloride is an exception. It might be expected that this curve would lie between the barium and calcium chloride curves, whereas it is found that strontium chloride is more effective in increasing the rate of hydrolysis than either of these salts. However, it does not seem to be an exaggeration to say that the increase in the hydrolytic action of the hydrochloric acid roughly parallels the activity coefficient of the hydrogen ion in these acid-chloride mixtures. It has been shown by Corran and Lewis[11] that the activity of the hydrogen ion is affected by the presence of sucrose. This is further discussed by Corran[12] and by Scatchard,[13] who concludes that the uncertainty as to the activity of the hydrogen ion in solutions containing sucrose makes inconclusive the attempts to obtain a quantitative relationship between reaction velocity and hydrogen activity. But in acid-salt-sucrose mixtures, especially



+, KCl; ○, NaCl; △, LiCl; - - - - - -, activity coefficient; ———, velocity constant.

Fig. 1.

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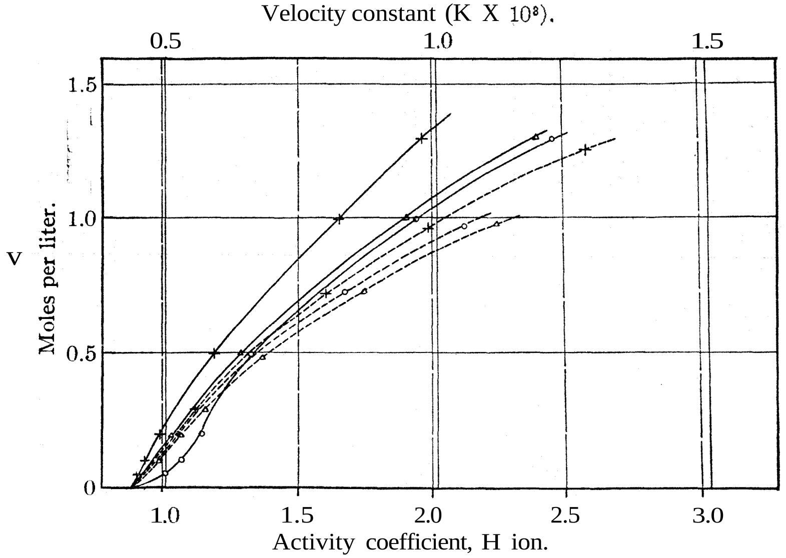
[11] Corran and Lewis, This Journal, 44, 1673 (1922).

[12] Corran, *ibid.*, 45, 1627 (1923).

[13] Scatchard, *ibid.*, 48, 2026 (1926).

at high salt concentrations, there is no doubt that the effect of the salt on the hydrogen ion activity predominates over the sucrose effect, and there seems to be some qualitative agreement between our results and this conclusion.

According to Brönsted[14] the cane sugar inversion, which he formulates, $C_{12}H_{22}O_{11} + H_3O^+ =$, as a reaction between a neutral molecule **and** a univalent ion, shows a very small salt effect in dilute solutions and, furthermore, the effect is proportional to the salt concentration. At our lowest salt concentrations, 0.05, 0.10 and 0.20 *M*, we found this proportionality to exist only for the lithium chloride solutions. Certainly at higher salt concentrations the salt effect is not small (from 50 to 100% at 1 M). Bronsted states that the small, linear effect of salts like sodium chloride on the catalysis by hydrochloric acid in dilute solutions shows that the activity of the hydrogen ion is not the determining factor. This effect is evidence in favor of this theory of ionic reactions which postulates the formation of a "critical complex" by the reacting ions or molecules as the determining factor. Attempts to test the activity theory in strong salt solutions are not justified, he believes, because the changes of the solvent due to the great concentration of salt have obscured the simple activity



+, BaCl₂; ○, SrCl₂; △, CaCl₂; ----, activity coefficient; ——, velocity constant.

Fig. 2.

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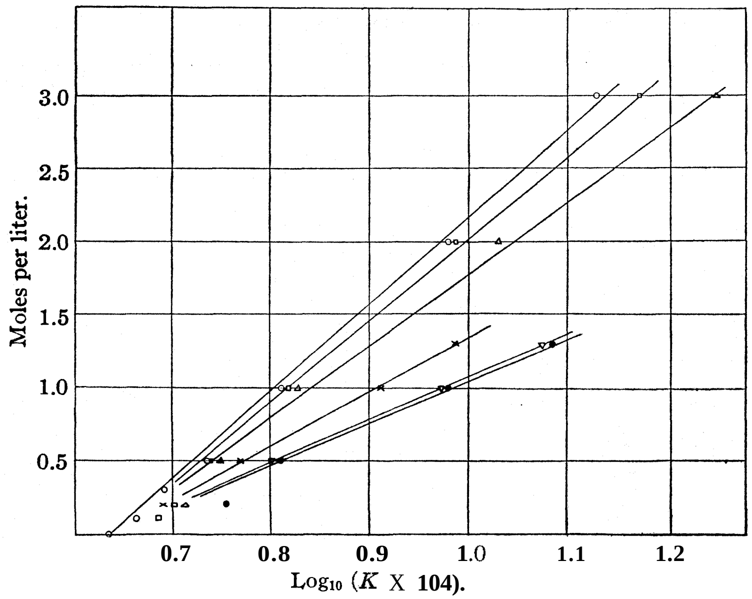
[14] Bronsted, *Z. physik. Chem.*, 102, 169 (1922), and "Contemporary Developments in Chemistry," Columbia University Press, 1927.

effect. Hückel's[15] extension of the theory of Debye and Hückel,[16] however, to concentrated solutions, taking into account in a formal way the effect of solvent changes on the activity coefficients of ions, seems to justify and encourage such a comparison.

If the dehydration of the H_3O^+ ions, or the displacement of the water equilibrium (equilibrium between mono-, di- and tri-hydrol) is the chief effect of the added salt,[4] then the various chlorides might be expected to influence the activity of the hydrochloric acid in the order of their hydration. The most recent data on the hydration of the alkali and alkaline earth chlorides[17] indicate that, of the alkali chlorides, lithium is the most strongly hydrated and potassium the least, which is in agreement with the order of their influence on the activity coefficient and hydrolytic action of the hydrogen ion. Strontium and calcium chlorides have practically the same hydration numbers up to 2 N; barium chloride is less hydrated.



○, KCl; □, NaCl; △, LiCl; X, $BaCl_2$; ●, $SrCl_2$; ▽, $CaCl_2$.

Fig. 3.

Harned[18] has examined certain data of Rivett on the acid hydrolysis of chlorylacetanilide to *p*-chloro-acetanilide in the presence of salts, and in this case also strontium chloride shows a greater effect than calcium

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[15] Hiickel, *Physik. Z.*, 26, 93 (1925).

[16] Debye and Hiickel, *ibid.*, 24, 185, 305 (1923).

[17] Sugden, *J. Chem. Soc.*, 129, 174 (1926).

[18] Harned, THIS JOURNAL, 40, 1461 (1918).

or **barium** chloride. The data obtained by us show the accelerating effect of the salts to be of the same order as in the work quoted.

Curves are also plotted using molar concentration of salt as abscissas **and** the logarithm of the velocity constants as ordinates in Fig. **3.** For agreement with the equation of Schmid and Olsen straight lines should be obtained. The equation holds fairly well for concentrations of salt above 0.5 M, particularly for the alkaline earth chlorides.

This equation seems derivable from the Hückel expression for the activity coefficient of an ion in concentrated solutions, with certain assumptions. The activity coefficient of the H^+ ion in 0.1 N hydrochloric acid is

$$\log \gamma_{H^+} = \frac{-a\sqrt{\mu}}{I + A\sqrt{\mu}} \qquad (1)$$

where a is a theoretical constant, A is a constant which depends on the mean distance of approach of the ions and μ is the ionic strength. The activity coefficient of the H^+ ion in concentrated solutions is, according to Hiickel.

$$\log \gamma_{H^+} = \frac{-a\sqrt{\mu_s}}{I + A\sqrt{\mu_s}} + B\mu_s \qquad (2)$$

where μ_s is the ionic strength at the particular concentration of added salt and B represents the effect of the ions on the dielectric constant of the solvent. The activity of the H^+ ion at any concentration C (in these experiments 0.1 N) is

$$\log f_{H_0^+} = \frac{-a\sqrt{\mu_0}}{I + A\sqrt{\mu_0}} + \log C \qquad (3)$$

and the activity of the H^+ ion at the same concentration in the presence of other ions is

$$\log f_{H^+} = \frac{-a\sqrt{\mu_s}}{I + A\sqrt{\mu_s}} + B\mu_s + \log C \qquad (4)$$

If, at high concentrations, the change in the dielectric constant of the medium determines γ and f (the first term of the right side of (4)) is neglected in comparison with the second term, then the activity of the H^+ ion in strong salt solutions is related to the activity of the H^+ ion of the same concentration, but with no added salt, in this way

$$\log f_{H^+} - \log f_{H_0^+} = B\mu_s + \frac{a\sqrt{\mu_0}}{I + A\sqrt{\mu_0}} \qquad (5)$$

The second term of the right side of *(5)* is small for strong acids at low concentrations; dropping this term brings *(5)* into conformity with the equation of Schmid and Olsen, which may be written

$$\log K = \log K_0 + rC$$

Summary

The rate of inversion of sucrose by 0.100 N hydrochloric acid, at 25°, in the presence of potassium, lithium, sodium, calcium, strontium and barium chlorides of concentrations from 0.05 to **3** N, has been determined.

No simple relationship was found to exist between the increased rate of inversion in the presence of these salts and the activity coefficients of the hydrogen ion in solutions of the same acid and salt concentrations containing no sucrose, but the rough parallelism observed indicates that the activity of the hydrogen ion is probably the most important factor in determining the rate of inversion.

For concentrations of salt above 0.500 M an equation proposed by Schmid and Olsen as describing the neutral salt action, $K = K_0 \times 10^{r'C}$, has been found to apply fairly well.

The equation of Schmid and Olsen is derived from the Hiickel expression for the activity coefficient of an ion in concentrated solutions, with certain assumptions. This also indicates the importance of the activity of the hydrogen ion in determining the rate of inversion.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

A MICRO CALORIMETER

BY S. G. LIPSETT, F. M. G. JOHNSON AND O. MAASS

RECEIVED DECEMBER 28, 1927 PUBLISHED APRIL 5, 1928

In this paper is described a small calorimeter with which heats of solution may be determined using only 4 cc. of solvent and corresponding amounts of solute. The heat capacity of the calorimeter itself is approximately 1 calorie. The calorimeter in all its essential details resembles very closely a larger calorimeter which was developed in this Laboratory in connection with work on the surface energy of solid sodium chloride.[1]

For a complete description of the construction and manipulation of this type of calorimeter, the reader is referred to these two papers. The following brief description may, however, be given here. The calorimeter, which is cylindrical in shape and closed at both ends, is placed with its axis horizontal and is able to revolve on an axle at each end. A separate vessel inside the calorimeter contains the solute, this vessel being surrounded by the solvent. On rotation, the solute and solvent mix. The adiabatic method of calorimetry is used. The calorimeter is enclosed in a copper jacket and the whole submerged in a bath of water (about 14 liters). By means of a radiation thermel placed in the air space between the calorimeter and the copper jacket, the temperature of the bath of water is kept always at the same temperature as the calorimeter. The actual temperature of the calorimeter is then determined by means of a platinum resistance thermometer placed in the bath of water.

[1] (a) Lipsett, Johnson and Maass, THIS JOURNAL, 49, 925 (1927); (b) Lipsett, Johnson and Maass, *ibid*, 49, 1940 (1927).

Description of Calorimeter.—The body of the calorimeter (A, Fig. 1) was made from a platinum crucible which was spun into the required shape. The lid of the crucible was flattened to form the removable end of the calorimeter. This body was cylindrical in shape, 2.2 cm. long and 2.5 cm in diameter. It was flanged at one end, B. The end, C, which was removable, consisted of a flat disk of platinum carrying an axle in the center. This disk was fastened to the flange, B (which was first coated with a thin film of vaseline), by means of 15 small steel screws (Waltham "Plate Screws" No. 131, size 18). The glass axles on which the calorimeter was supported were 1 mm. in diameter. A piece of brass, D, was cemented to one axle and into this could be screwed a long steel axle, by means of which the calorimeter was rotated.

The solute was placed in a small platinum box, E, which was also cylindrical in shape, 1.7 cm. long and 1.5 cm. in diameter, having a capacity of 2.7 cc. This box was made to slip into the calorimeter, where it was held in position by thin platinum supports projecting from the sides and bottom of the box. The bottom support, F was forked and fitted over a small platinum projection, G, in the body of the calorimeter. In the top of the box was an opening 6 X 9 mm. The opening was flanged and on the flange the lid of the box rested. The lid was a small piece of platinum 12 × 9 X 1.3 mm., ground plane on one side, weighing 4 g. When the flange of the box was moistened with glycoline and the lid placed on, the solute inside the box was protected from any possible action of solvent vapor. The solvent was introduced into the calorimeter through the opening, H, which was closed by a tapering platinum plug.

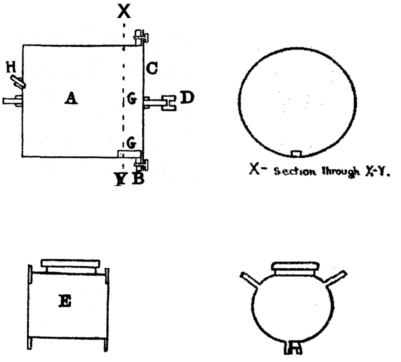

Fig. 1.

On rotation of the calorimeter, the lid of the inner box fell off and solution of the solute took place.

TABLE I

THE HEAT CAPACITY OF THE CALORIMETER AT 25°

Material	Quantity	Spec. heat, cal.	Heat capacity, cal.
Platinum	32.56 g.	0.0314[a]	1.0224
Glass[b]	0.014 g.	.18	0.0025
Steel screws	.429 g.	.107	.0459
Air inside calorimeter	4.5 cc.	....	.0010
Air in gap[c]	16 cc.	....	.0040
Glycoline, vaseline	0.014 g.	.45	.0061
Gold[d]	.245 g.	.0316	.0077
Total heat capacity			1.090

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[a] White, *Phys. Rev.*, 12, 436 (1918); Gaede, *Physik. Z.*, 4, 105 (1902); Schlett, *Ann. phys.*, [4] 26, 201 (1908). This value may be high, as Schlett has shown that hammering decreases the specific heat of platinum.

[b] Half the weight of the glass axles is taken.

[c] The volume considered is that portion estimated to be effective in heating the calorimeter.

[d] Used as solder.

The calorimeter was enclosed in a copper jacket in exactly the same manner as the previously used calorimeter[1] except that the air gap in the present case was only 6 mm. in width. The inside of the copper jacket was gold plated to reduce radiation of heat. The radiation thermel was similar to the one used previously.[2]

The accessory apparatus, namely, outer bath, resistance thermometer, bridge, galvanometer, etc., was the same as had been used before.

Heat Capacity of the Calorimeter.—The heat capacity of the calorimeter was calculated as shown in Table I.

Experimental Part

The large surface of the calorimeter compared to its heat capacity offered opportunity for large errors if the adiabatic control was not accurately maintained. It was found that when the environment was kept 1° hotter than the calorimeter, the temperature of the latter rose at the rate of 0.04° per minute when the calorimeter contained 4 cc. of water. Except for one minute, however, when the solute and solvent were first mixed, the temperature difference between the calorimeter and surrounding jacket was usually so small that, except during this minute, errors due to loss or gain of heat from the environment were negligible. During the greater part of an experiment this temperature difference was less than 0.0002°.

During the solution of the solute, the calorimeter was rotated for ten minutes at the rate of 10 r.p.m. It was found that the heat generated by friction during rotation was sufficient to cause a rise in temperature of the calorimeter and contents (which had a total heat capacity of approximately 5 cal.) of about 0.00015° per minute.

The calorimeter was tested by making several determinations of the heat of solution of sodium chloride at 25°, obtaining in each case a 9.114% solution. For this purpose approximately 0.4 g. of salt was used and dissolved in 4 cc. of water. The change in temperature which was measured was approximately 1°.

TABLE II

HEAT OF SOLUTION OF SODIUM CHLORIDE AT 25°

Expt.	Heat of solution, cal. per mole (9.114% soln.)	Deviation from mean, %
1	790.1	0.06
2	788.4	.15
3	788.1	.19
4	791.6	.25
5	787.8	.23
6	791.7	.26
Mean	789.6	

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[2] It was erroneously stated (ref. 1 a, p. 929) that the thermel was made from wire 0.02 mm. in diameter, rolled flat till about 0.8 mm. wide and 0.03 mm. thick. The original diameter should have read 0.02 cm. instead of 0.02 mm.

The results appear in Table II. The corrections used in **making the** calculations have been described in the previous papers.

It will be seen that the maximum deviation from the mean value is 0.26%.

The heat of solution of sodium chloride under the same conditions, as determined with the former calorimeter,[1b] was 787.5 cal. per mole. The difference between this and the above results may easily be accounted for by the uncertainty in the values used for the specific heats of the sterling silver and the platinum from which the calorimeters were constructed.

The results obtained show that a fair degree of accuracy may be attained with a calorimeter of this type while requiring the use of only small quantities of material.

Grateful acknowledgment is made to the National Research Council of Canada for a grant to aid in this research and also for a Studentship held by one of us, during the tenure of which the work was carried out.

Summary

A small calorimeter is described with which heats of solution may be determined using 4 cc. of solvent and corresponding amounts of solute. The heat capacity of the calorimeter is approximately 1 cal.

Several determinations of the heat of solution of sodium chloride at the same concentration gave results which never differed from a mean value by more than 0.26%.

MONTREAL, CANADA

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF BRYN MAWR COLLEGE AND THE CHEMICAL LABORATORY OF THE U. G. I. CONTRACTING COMPANY]

THE NEAR INFRA-RED ABSORPTION BANDS OF SOME HYDROCARBONS

BY JAMES BARNES AND W. H. FULWEILER

RECEIVED DECEMBER 30, 1927 PUBLISHED APRIL 5, 1928

This report, which is a continuation of earlier papers,[1] is on the measurements of the wave lengths of the near infra-red absorption bands of liquid pentane, decane and tetradecane. It also contains some observations on the structure of the 8744 Å. band of benzene and the 8767 Å. band of toluene.

The apparatus used, namely, source of continuous radiation, cells, gratings and densitometer, as well as the methods of photography and of measurement of wave lengths, were the same as those described in the papers referred to above. In addition, a Hilger prism spectrometer of

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[1] Barnes and Fulweiler, THIS JOURNAL, 49, 2034 (1927); J. Opt. *Soc. Am.*, 15, 331 (1927).

the constant deviation type D with camera attachment was employed. Due to its low dispersion, results of importance were observed which did not appear on the plates obtained with the gratings. We also used to advantage a filter[2] of solarized green celluloid which Dr. Pettit of Mt. Wilson Observatory kindly sent to us.

On account of the diffuseness of the absorption bands of the paraffins compared with those of the benzene derivatives, the measurements of their wave lengths are not quite so accurate but are believed to be within 20 Å. or 0.002μ. We have, therefore, recorded the following results using μ instead of Å. as the unit. They are the means of many measurements made upon the center of the bands from a number of photographic plates, never less than two, of each substance in cells 30 and 80 cm. long.

Each of the two strongest absorption bands of the paraffins in the region investigated is a doublet whose component wave lengths will be designated by λ_1 and λ_2, and their frequencies by ν_1 and ν_2, the difference of which, Av, is given in the fifth column of figures in Tables I and II, where the measurements were made on plates taken with the plane grating and the six-foot concave grating.

Results

Table I gives the results for the absorption band at 0.92μ, approximately.

TABLE I

WAVE LENGTHS AND FREQUENCIES OF THE 0.92μ BAND OF PARAFFINS

	$\lambda_1(\mu)$	$\lambda_2(\mu)$	$\nu \times 10^{-12}$	$\nu \times 10^{-12}$	$A\nu \times 10^{-12}$
Pentane	0.912	0.932	329	322	7
Decane	.913	.936	328	321	7
Tetradecane	.914	.934	328	321	7

Table II gives the results for the absorption band at 0.75μ, approximately.

TABLE II

WAVE LENGTH AND FREQUENCIES OF THE 0.75μ BAND OF PARAFFINS

	$\lambda_1(\mu)$	$\lambda_2(\mu)$	$\nu \times 10^{-12}$	$\nu \times 10^{-12}$	$\Delta\nu \times 10^{-12}$
Pentane	0.745	0.760	403	395	8
Decane	.747	.763	401	393	8
Tetradecane	.747	.763	401	393	8

These tables show that the frequencies of the bands of the hydrocarbons of the paraffin series are lower than the frequencies of the corresponding bands of the benzene series, and that the frequencies tend to decrease as the mass of the molecule becomes larger, which is also the case with the benzene series. They also show that the frequency difference, Av,

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[2] Pettit, *Astrophys.* J..66, 46 (1927).

which is of interest for the calculation[3] of the moments of inertia of the molecules, depends on the order of the band in the series, if one assumes that these bands are due to an unharmonic rotational and vibrational oscillator in the molecule. In this connection, the results obtained by Meyer, Bronk and Levin[4] for gaseous butane, hexane and octane are worthy of comparison with the above.

As is usually the case with the so-called vibrational-rotational bands in gases, the shorter wave length component in both the above bands in all three liquid paraffins has the stronger intensity, the densitometer graphs giving their relative intensity as very nearly 4 to 3.

Using the prism spectrometer with cells 80 cm. in length, the paraffins showed, in addition to the above strong, double bands, two weak single bands with wave lengths approximately 0.81μ and 0.97μ. The accurate measurement of these bands will require much longer absorption cells than those used up to the present time. However, it is important to note that under similar conditions the benzene derivatives do not show a corresponding series.

The slopes of the curves on the densitometer graphs of the strong absorption bands 8744 Å. of benzene and 8767 Å. of toluene suggested that they also were doublets, the details of which were lost due to the large dispersion of the gratings. Plates were therefore taken with the prism spectrometer of the absorption of these two liquids in cells of 80 cm. length and they showed clearly the results as predicted. The differences in their frequencies, $\Delta\nu$, were the same within the limit of measurement and had a value of 3×10^{12} sec.$^{-1}$. With the same length of cell the benzene band at 7133 Å. and the toluene band at 7142 Å. showed no sign of doubling.

Summary

The near infra-red absorption bands of liquid pentane, decane and tetradecane, which were photographed with grating and prism spectrometers, were each found to consist of a doublet and a singlet series. The frequencies of the doublet series of the paraffins were lower than the frequencies of the corresponding series of the benzenes. The frequency difference for the paraffin doublet band at 0.92μ was 7×10^{12} sec.$^{-1}$, while for the band at 0.75μ it was 8×10^{12} sec.$^{-1}$.

The 0.874μ band of benzene and the 0.877μ band of toluene are also close doublets with a frequency difference of 3×10^{12} sec.$^{-1}$.

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[3] Kemble, "Molecular Spectra in Gases," *Bulletin National Research Council,* 1926, p. 11 et *seq.*

[4] Meyer, Bronk and Levin, *J. Opt. Soc. Am.*, 15,257 (1927).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY. CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 160]

THE INFLUENCE OF RELATIVE IONIC SIZES ON THE PROPERTIES OF IONIC COMPOUNDS

BY LINUS PAULING

RECEIVED JANUARY 4, 1928 PUBLISHED APRIL 5, 1928

Introduction

The simple method used by Born[1] to calculate the crystal energy of an ionic crystal has been widely applied for evaluating the electron affinities of atoms, the heats of solution of ions and in other similar problems in chemical thermodynamics. The repulsive potential is assumed to vary inversely with a high power of the interionic distance, so that the crystal energy per molecule may be written

$$\Phi = -\frac{z^2e^2A}{r} + \frac{B}{r^n} \tag{1}$$

in which ze is the charge of an ion, r a characteristic interionic distance, and A and B are constants for a given crystal. The Madelung constant A may be calculated for any given ionic arrangement from the laws of electrostatics, and B is chosen so that at equilibrium, where $d\Phi/dr = 0$, r will have the value R found experimentally for the crystal under consideration. The crystal energy at equilibrium is

$$U = -\frac{z^2e^2A}{R}\left(1 - \frac{1}{n}\right) \tag{2}$$

The repulsion exponent n is usually placed equal to 9, an average of the values obtained from the experimentally measured compressibilities of the alkali halides.

For the theoretical treatment of many phenomena it is necessary to know the relative magnitude of the repulsive forces between unlike ions and those between like ions. Moreover, it is often desired to make calculations for non-existent crystals, or other crystals for which R (and hence B) has not been experimentally determined. With the development of our knowledge of the sizes of ions it has become possible to express the interionic forces in a crystal in terms of radii of the ions in the crystal.[2] The resultant equation for the crystal energy is of the type of Equation 1, and it has the same limits of accuracy (1 or 2%). Like Born's equation, it is held to represent the actual crystal only to a first approximation; and it cannot be used in treating second order effects. On applying the equation it has been found that many properties of crystals depend not only on the distance between neighboring ions in the crystal (the

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[1] Born, "Atomtheorie des Festen Zustandes," Teubner, 1923, p. 749.

[2] A detailed account of this work is given in a paper to be published in the *Z. Krist.* The present article contains only a description of the applications of interest to chemists.

"radius sum"), but also on the *relative* sizes of cation and anion (the "radius ratio"). The previously unrecognized effect of the radius ratio has been shown to account for a number of irregularities in the properties of the alkali halides formerly adduced as evidence for the existence of important deformation phenomena.

The Alkali Halides: Deviation of Interionic Distances from Additivity

By applying the perturbation theory of the new quantum mechanics to a simple model susceptible to quantitative treatment, it can be shown that the potential energy of two ions A and B, a distance r_{AB} apart, may be approximately written (neglecting polarization) as

$$\varphi = \frac{z_A z_B e^2}{r_{AB}} + \beta_{AB}\frac{(r_A + r_B)^n}{r_{AB}^n}\cdot B_0 \qquad (3)$$

in which r_A and r_B are "standard radii" characteristic of the ions, B_0 is a constant for all ions, and β_{AB} has certain values obtained from the model (in particular, 1 for $M^+ - X^-$, 0.75 for $X^- - X^-$ and 1.25 for $M^+ - M^+$). On introducing this expression for the potential energy of each pair of ions in a sodium chloride type crystal (taking into consideration the repulsive potential between each ion and the adjoining six unlike and twelve like ions), there results for the equilibrium interionic distance R, the equation

$$R = (r_+ + r_-)^{\frac{n}{n-1}}\cdot F(\rho) \qquad (4)$$

with

$$F(\rho) = \left\{\frac{(1+\rho)^n + \beta_{++}(\sqrt{2}\,\rho)^n + \beta_{--}(\sqrt{2})^n}{(1.75)^n + \beta_{++}(\sqrt{2}\cdot 0.75)^n + \beta_{--}(\sqrt{2})^n}\right\}^{\frac{1}{n-1}} \qquad (4a)$$

in which B_0 and the standard radii have been so chosen that $R = (r_+ + r_-)^{\frac{n}{n-1}}$ for the radius ratio ρ equal to 0.75. This function, calculated for $\beta_{++} = 1.25$, $\beta_{--} = 0.75$ and $n = 9$, is represented in Fig. 1.

The deviation of interionic distances in the alkali halide series from additivity is well known.[3] The most pronounced deviations, those of the lithium salts, were explained by Landé[4] and Wasastjema[5] as arising from the mutual contact of the anions; if the ions are considered as rigid spheres, contact between the anions occurs for $\rho = 0.414$, causing the interionic distance to increase as shown by the broken line in Fig. 1. It has also been pointed out[6] that for actual mutually repelling ions an increase in the interionic distance will take place at values of ρ even somewhat larger than 0.414, for repulsion both between anion and cation and

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[3] See Fajans and Grimm, *Z. Physik*, **2**, 299 (1920); Fajans and Herzfeld, *ibid.*, **2**, 309 (1920).

[4] Landé, *ibid.*, 1, 191 (1920).

[5] Wasastjerna, *Soc. Sci. Fenn. Comm. Phys. Math.*, 38, 1 (1923).

Pauling, THIS JOURNAL, **49**, 765 (1927).

between anion and anion will be operative; this effect of "double repulsion" provides a qualitative explanation of further deviations from additivity shown by the alkali halides. It will be seen from Fig. 1 that the quantitative considerations of this paper substantiate these views. $F(\rho)$ is roughly unity for ρ larger than 0.70; it approximates the anion-contact curve for small values of ρ, and for values in the neighborhood of 0.414 it is considerably higher than the rigid-sphere curve, showing the effect of double repulsion.

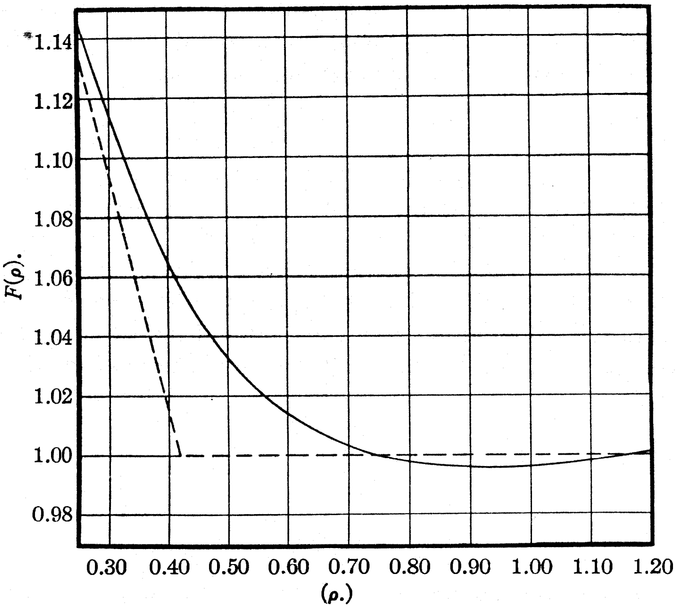

Fig. 1.—The correction factor $F(\rho)$ giving the dependency of interionic distance in sodium chloride type crystals on the radius ratio ρ (solid line). The broken line shows the form of this function for $n = \infty$; that is, for solid spheres.

It is, moreover, possible to select values of r_+ and r_- for the alkali and halide ions such that the interionic distances as calculated by Equation 4 are in complete agreement with experiment for all the alkali halides. In this calculation n was given the value 9 and β_{++} and β_{--} the values 1.25 and 0.75 throughout. The values of r_+ and r_- used are given in Table I.

TABLE I

STANDARD RADII FOR THE ALKALI AND HALIDE IONS

	r_+, Å.		r_-, Å.
Li^+	0.574		
Na^+	0.873	F^-	1.225
K^+	1.173	Cl^-	1,589
Rb^+	1.294	Br^-	1.702
Cs^+	1.434	I^-	1.867

Those for K^+ and Cl^- and for Rb^+ and Br^- were chosen such that their ratios agree with the ratios of previously derived size screening constants,[7] and the remaining r's were then taken to cause agreement with the experimental data.

TABLE II

THE RADIUS RATIO ρ, THE CORRECTION FACTOR $F(\rho)$ AND THE CORRECTED INTERIONIC DISTANCE $R_{0.75}$ FOR THE ALKALI HALIDES

		F^-	Cl^-	Br^-	I^-
Li^+	ρ	= 0.464	0.357	0.334	0.304
	$F(\rho)$	= 1.042	1,082	1.094	1.111
	$R_{0.75}$	= 1.927 Å.	2.373 Å.	2.513 Å.	2.720 Å.
Na^+	ρ	= 0.713	0.550	0.513	0.468
	$F(\rho)$	= 1.002	1 023	1.029	1.041
	$R_{0.75}$	= 2.302 Å.	2.753 Å.	2.894 Å.	3.106 Å.
K^+	ρ	= 0.959	0.739	0.689	0.629
	$F(\rho)$	= 0.995	1.001	1.006	1 010
	$R_{0.75}$	= 2.675 Å.	3 138 Å.	3 278 Å.	3.494 Å.
Rb^+	ρ	= 1.057	0 815	0.760	0.694
	$F(\rho)$	= 0.997	997	.999	1.004
	$R_{0.75}$	= 2.827 Å.	3 288 Å.	3 436 Å.	3.650 Å.
Cs^+	ρ	= 1.172	0 903	0.843	0.769
	$F(\rho)$	= 0.999	.995	.996	.999
	$R_{0.75}$	= 3.008 Å.	3.471 Å.	3.617 Å.	3.832 Å.

The corresponding values of the radius ratio and of the correction factor $F(\rho)$ for the alkali halides are given in Table II. In addition there are given values of $R_{0.75}$ obtained from Equation 4 by placing $F(\rho) = 1$. These are the interionic distances the crystals would show if the radius ratio effect did not exist. By multiplying $R_{0.75}$ by $F(\rho)$ we obtain the calculated values of the interionic distance in the alkali halides as given by Equation 4. For comparison the calculated and observed values are given together in Table III.

TABLE III

MEASURED AND CALCULATED INTERIONIC DISTANCES IN THE ALKALI HALIDE CRYSTALS[a]

	F^-, Å.	Cl^-, Å.	Br^-, Å.	I^-, Å.
Li^+	2.008	2 567	2 747	3.022
	2.009	2.566	2.745	3.025
Na^+	2.307	2.815	2.979	3.233
	2 310	2.814	2 981	3.231
K^+	2.663	3 140	3 293	3.527
	2.664	3.140	3.293, 3.289	3.526
Rb^+	2.817	3 277	3.434	3.663
	2.815	3.268, 3.285	3.434	3.663
Cs^+	3.005	3.455	3.604	3.828
	3.005	(3.560)[b]	(3.715)[b]	(3.95)[b]

[a] The upper figure in each case is the calculated one. For literature citations see ref. 2.

[b] Cesium chloride structure.

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[7] Pauling, Proc. Roy. *Soc.* (London), **114A,** 181 (1927); THIS JOURNAL, 49, 765 (1927).

The average difference is ±0.001 Å., within the experimental error, so that the agreement can be said to be complete. The deviations from additivity to be accounted for are as large as 0.150 Å., and in the case of lithium iodide the correction due to $F(\rho)$ is 0.302 Å. No arbitrary parameters other than the r's were introduced in this calculation, for n, β_{++} and $\beta_{=}$ were previously determined. Hence by means of nine variables (the r's) seventeen equations giving the interionic distances are satisfied, as well as the two equations giving the previously determined ratios r_+/r_- for K^+/Cl^- and Rb^+/Br^-. This may be compared with the results of Fajans and Herzfeld, who, using the model of the static cubical ion, calculated eleven interionic distances (not including the lithium salts, which show the greatest deviation) with an average error of 0.004 Å. by the use of seven arbitrarily chosen radii.

The calculated values for the cesium halides give closely the distances to be expected for these substances crystallizing with the sodium chloride structure. Under ordinary conditions these salts (except the fluoride) have the cesium chloride arrangement, with the interionic distances shown in the table. The increase in R in going from the sodium chloride to the cesium chloride structure is from these figures, 3.03, 3.08 and 3.19% for the chloride, bromide and iodide of cesium, agreeing with the increase of 3% deduced by Goldschmidt[8] from the measured distances in the two forms of the ammonium halides. The theoretical interpretation of this increase is discussed elsewhere.[2]

Melting Points, Boiling Points and Related Properties

The effect of the radius ratio on other properties of the alkali halides can be similarly discussed. In some cases the radius ratio is of no importance; thus the interatomic distance in a gaseous diatomic salt molecule is not a function of it (for only the radius sum enters in the equation expressing the potential energy of two ions), nor is the energy of formation of such a molecule from free ions. In order to separate the effect of the radius ratio from other effects we shall define for each substance a corresponding hypothetical standard substance; namely, one with the same radius sum $r_+ + r_-$, and the same ionic properties otherwise, but with the standard radius ratio $\rho = 0.75$. The properties attributed to this hypothetical substance will be designated as corrected for the radius ratio effect or, briefly, corrected.

The effect of the radius ratio on interionic distances is shown in Fig. 2, in which the actual interionic distances (Table III) are connected by solid lines, and the corrected ones ($R_{0.75}$ of Table II) by broken lines. It will be seen that the corrected distances show some regularities not exhibited

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[8] Goldschmidt, *Skrifter Det Norske Videnskaps-Akademi i Oslo. 1926, No. 2;* 1927, No. *8.*

by the actual ones; thus the approximate equality of the differences Cs^+–Rb^+ and Rb^+–K^+ is shown also by the much larger differences K^+–Na^+ and Na^+–Li^+.

The related properties density and molecular volume are, of course, also similarly affected by the radius ratio, the percentage corrections being roughly three times as large as those for the interionic distances.

The properties to be expected of the hypothetical alkali halides with $\rho = 0.75$ are the following. The interionic distances in the crystals should conform nearly to additivity, as is shown in Fig. 2. The crystal energy, which is inversely proportional to the interionic distance, should show a corresponding regularity. A large number of properties of salts depend essentially on the crystal energy—the heat of fusion, heat of sublimation, melting point, boiling point, solubility, etc. All of these properties in the case of the hypothetical alkali halides would exhibit a regular dependency on the interionic distance, and hence the curves showing any one of these properties should be similar to the dotted lines in Fig. 2. The properties of the actual alkali halides deviate very much from this expected regularity; the observed melting points, for example, shown on the left side of Fig. 3, deviate greatly from inverse proportionality with the interionic distances.

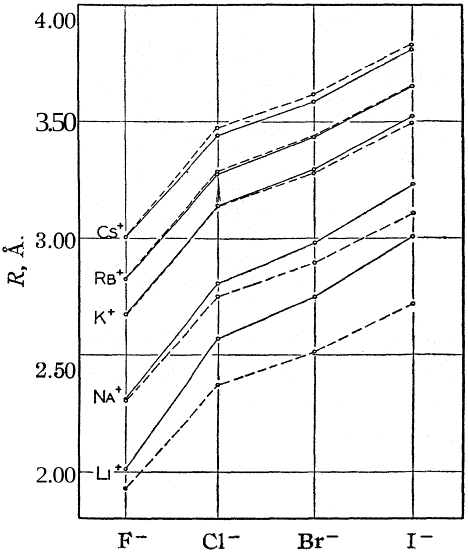

Fig. 2.—The points connected by solid lines give the actual interionic distances for alkali halide crystals with the sodium chloride arrangement, and those connected with broken lines interionic distances corrected for the radius ratio effect; that is, calculated for hypothetical substances with the same radius sums as the alkali halides but with the standard radius ratio $\rho = 0.75$.

The quantitative explanation of such discrepancies is again provided by the radius ratio effect. The crystal energy of each hypothetical alkali halide with $\rho = 0.75$ (the corrected crystal energy) and that of the actual crystal may be obtained from Equation 2 with the aid of the data of Tables II and III. The difference ΔU between the actual and the corrected crystal energy is given by the equation

$$\Delta U = -z^2e^2 A \left(1 - \frac{1}{n}\right)\left(\frac{1}{R} - \frac{1}{R_{0.75}}\right)$$

Values of this quantity are given in Table IV.

TABLE IV

THE EFFECT OF THE RADIUS RATIO ON CRYSTAL ENERGY, BOILING POINTS AND MELTING POINTS

		F^-	Cl^-	Br^-	I^-
Li^+	ΔU =	10.8	16.4	17.6	18.8
	ΔT_{BP} =	138°	209°	225°	240°
	ΔT_{MP} =	270°	410°	440°	470°
Na^+	ΔU =	0.5	4.1	5.1	6.5
	ΔT_{BP} =	7°	52°	65°	83°
	ΔT_{MP} =	13°	102°	127°	162°
K^+	ΔU =	−0.9	0.1	0.7	1.4
	ΔT_{BP} =	−11°	1°	9°	18°
	ΔT_{MP} =	−22°	3°	18°	35°
Rb^+	ΔU =	−0.6	−0.5	−0.1	0.5
	ΔT_{BP} =	−8°	−7°	−1°	7°
	ΔT_{MP} =	−15°	−13°	−3°	13°
Cs^+	ΔU =	−0.2	−0.7	−0.5	−0.1
	ΔT_{BP} =	−3°	−9°	−7°	−1°
	ΔT_{MP} =	−5°	−18°	−13°	−3°

The energy difference ΔU is largest for lithium iodide, amounting to 11% of the total energy. The same energy quantity is required to correct the heat of sublimation, as the energy of a gaseous molecule is not a function of the radius ratio.

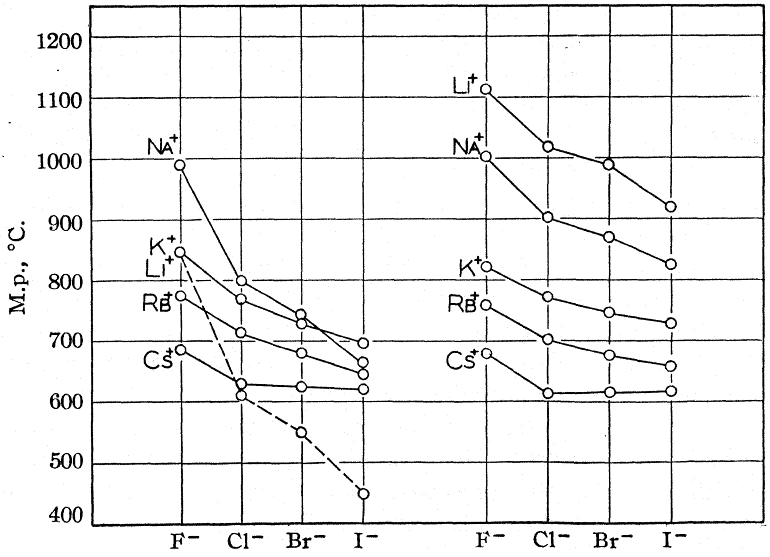

Fig. 3.—The points on the left are the observed melting points of the alkali halides; those on the right are corrected for the radius ratio effect.

The heat of sublimation at room temperature is equal to the sum of the heat of fusion at the melting point, the heat of vaporization at the boiling point and the difference between the heat capacity of the solid and liquid and that of the vapor, integrated from room temperature to the boiling point; so that these quantities are also subject to correction for the radius ratio effect. For potassium chloride 10% of the total heat of sublimation is heat of fusion, 60% heat of vaporization and 30% results from the heat-capacity difference. It would perhaps be reasonable to divide the correction energy in these proportions; however, it is to be expected that the transition from crystal to liquid would work to destroy the coördination character of the ionic aggregation, causing the heat of fusion to assume a larger share of the correction energy, and that furthermore the coordination surviving in the liquid would decrease rapidly with increasing temperature, so that the heat content of the liquid would also assume more than its share of ΔU.[9] The following calculations were made by apportioning 15% of ΔU to the heat of fusion and 30% to the heat of vaporization, these proportions being chosen partially to produce satisfactory results in the consideration below of boiling points and melting points.

These heat quantities themselves are not sufficiently accurately known throughout the series to provide material for the direct test of this effect. The boiling point of a substance is, however, related to its heat of vaporization by Trouton's rule, according to which the entropy of vaporization is a constant. For the alkali halides this constant has the value 23.5 cal./mole degree, found from the experimental values of the heat of vaporization and the boiling points. If the corrected boiling points be so calculated, then the correction, in degrees, is

$$\Delta T_{\text{BP}} = \frac{0.30\ \Delta U}{0.0235} \tag{5}$$

Similarly we may assume that the entropy of fusion is constant (Richards' rule), with the value 6.0 cal./mole degree. The resultant melting point correction is then

$$\Delta T_{\text{MP}} = \frac{0.15\ \Delta U}{0.0060} \tag{6}$$

The values of ΔT_{BP} and ΔT_{MP} obtained by the use of the previous results for ΔU are also given in Table IV.

The observed melting points and boiling points of the alkali halides[10] (Figs. **3** and 4, left side) show large irregularities, and correspond only very roughly with the crystal distances, to which, if the radius ratio be not considered, they should be closely related. Thus the boiling points

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[9] This would cause the salts for which ΔU is large to show low values of the heat capacity and of the thermal coefficient of expansion in the fused state.

[10] We apply these considerations also to the cesium salts, three of which have at room temperature the cesium chloride structure. This can, of course, have no effect on the boiling point; and it is furthermore probable that the salts undergo transformation to the sodium chloride structure before reaching the melting point.

and melting points of **all** the lithium salts lie below those of the corresponding sodium salts; those of lithium iodide being, in fact, the lowest of all for the alkali halides. These irregularities have been previously explained[11] as resulting from the influence of deformation of the ions in the gaseous molecule, which would tend to decrease the heat of sublimation and hence to lower the boiling point and melting point. Our calculations show, however, that they result mainly from the radius ratio effect. The corrected melting points (Fig. **3)** are entirely regular and correspond closely to the crystal distances. Indeed, since in the fused salt a coördination structure only somewhat less pronounced than that for the crystal exists, the electric field is extremely small at the center of each ion, and only poles of high order (no electric dipoles) will be formed; so that the heat of fusion and the melting point would not be expected to vary appreciably with the polarizability or deformability of the ions. On the other hand, some influence of the polarization of the ions in the vapor molecule on the heat of vaporization and boiling point is to be expected, although not so large as that previously postulated. The boiling points corrected for the radius ratio effect (Fig. 4) are not completely regular, even though a favorable value of the fraction of ΔU to be attributed to heat of vaporization has been chosen. It is not possible to eliminate the inverted order of the cesium halides by any choice of fraction of AU. This small residual effect is no doubt to be attributed to deformation.

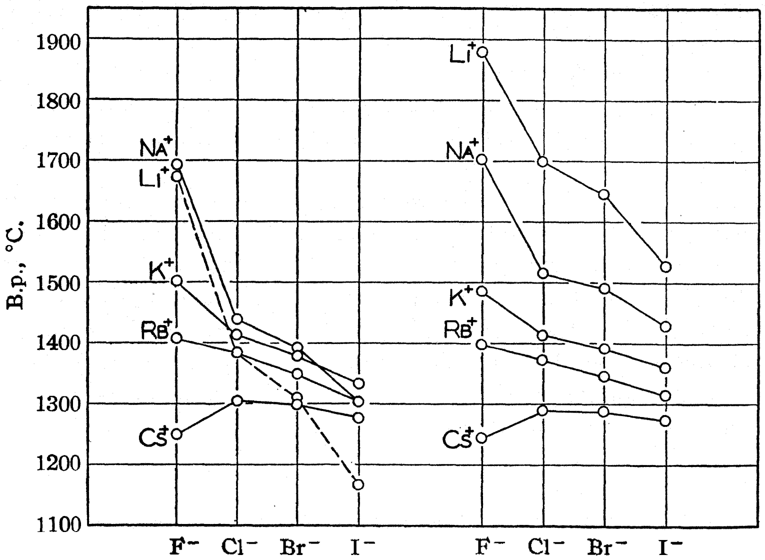

Fig. 4.—The points on the left are the observed boiling points of the alkali halides; those on the right are corrected for the radius ratio effect.

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[11] **Fajans, *Z. Krist.*, 61, 18 (1925).**

Thus we may conclude that the major anomalies in the melting points and boiling points of the alkali halides result from the influence of the relative sizes of cation and anion, and that deformation phenomena play only a minor role.

Further Radius Ratio Effects

The action of the radius ratio in influencing the axial ratio of tetragonal crystals with the rutile and anatase structures has been evaluated, and shown to agree well with the results of observation.[2] The radius ratio is also of significance for the relative stability of alternative crystal structures, for the variation of interionic distance accompanying transition from one structure to another,[2] for hydrate and ammoniate formation and for the solubility of salts; in short, for all properties dependent on the crystal energy. The potential expressions of this paper are now being applied to the problems of ion formation, valence and the structure of ionic complexes.

Summary

With the aid of an expression for the mutual energy of ions in terms of standard ionic radii it is shown that the ratio of cation radius to anion radius influences the properties of ionic substances. Irregularities in interionic distances, melting points and boiling points of the alkali halides are explained as resulting from this effect.

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[CONTRIBUTION FROM THE MARTIN MALONEY CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

ADSORPTION OF SULFUR DIOXIDE BY TITANIA GEL

BY SIMON KLOSKY AND A. J. BURGGRAFF[1]

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The object of this investigation was to determine whether a porous body similar to silica gel, but with a more specific attraction for sulfur dioxide, would adsorb it according to Patrick's condensation formula.

Material

The titania gel was prepared in quantity according to the method of Klosky and Marzano.[2] The sulfur dioxide was taken from the metal tanks which are sold in industry. Its purity was tested by absorbing a known volume in concentrated sodium hydroxide. The gas was completely adsorbed by the sodium hydroxide.

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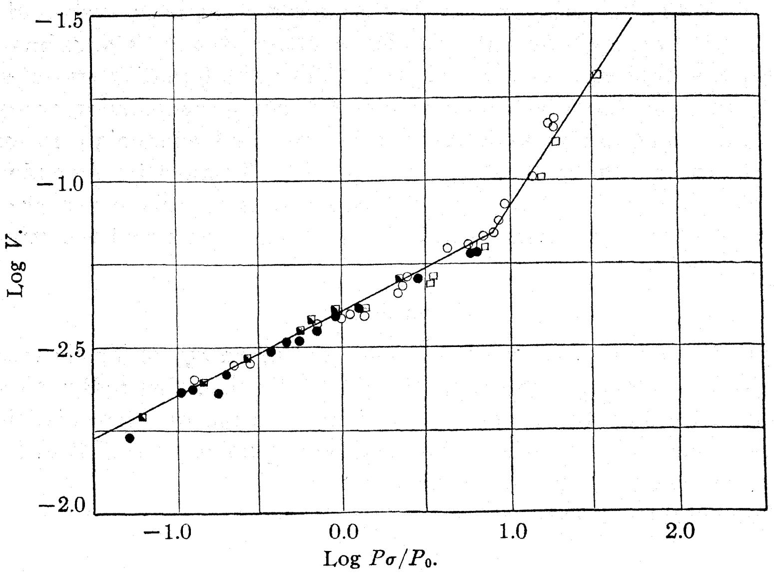
[1] Extract from Doctor's Dissertation, 1927.

[2] Klosky and Marzano, J. Phys. *Chem.*, *29*, 1125 (1925).

The Apparatus

The apparatus used was similar to that used by Patrick and Opdycke.[3] It consisted of flowmeters, which registered any fluctuation in the flow of air or sulfur dioxide above 0.01 cc. per second; a constant temperature bath in which were placed a large cooling coil, a U-tube containing the gel and a sample bottle for the analysis of effluent gases.



▨, 50°; ●, 25°; ○, 0°; □, −22.5°.

Fig. 1.

Manipulation

A mixture of sulfur dioxide and air of constant composition was passed over the gel until no further increase in weight was noticed. The effluent gases were passed through the sample bottle during the entire run. When equilibrium was reached, the U-tube was closed by means of stopcocks and weighed. The sulfur dioxide in the sample bottle was absorbed in a standard iodine solution and the excess iodine titrated with sodium thiosulfate. Knowing the volume of the sample bottle, the external pressure, the temperature of the mixture of gases and the amount of standard iodine solution required, the partial pressure of the sulfur dioxide could be calculated easily. The following table gives the results obtained for four isotherms, where x/m is the weight of sulfur dioxide adsorbed in grams per gram of gel and P is the partial pressure of the sulfur dioxide in millimeters.

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[3] Patrick and Opdycke, *J. Phys. Chem.*, **29**, 601 (1925).

TABLE I

EXPERIMENTAL RESULTS

−22 50°C.		0°C.		25°C.	
x/m (g./g.)	9 (mm)	x/m (g./g.)	p (mm.)	x/m (g./g.)	9 (mm.)
0.0621	17.35	0.0363	5.50	0.0236	6.60
.0680	17.33	.0400	9.50	.0320	13.20
.0745	42.50	.0405	12.10	.0326	15.70
.0762	43.20	.0535	28.62	.0310	23.60
.9440	78.60	.0565	40.80	.0368	25.98
.0973	93 60	.0584	46.40	.0420	47.50
.1580	185.0	.0690	98.00	.0447	58.00
.2000	253.0	,0736	102.5	.0450	68.00
.3160	440.0	.0824	179.0	.0480	74.00
		.0912	224.1	.0496	95.05
50 °C.		.0973	298.0	.0535	119.0
		.0980	338.6	.0575	158.7
.0226	9 80	.1095	344.0	.0558	164.0
.0266	21.40	.1120	374.0	.0655	271.5
.0326	48.40	.1568	592.0	.0700	362.5
.0385	93.50	.2200	720.0	.0845	758.0
.0470	190.4	.2220	760.0	.0 W	760.0
.0500	238 0	.2100	745.0		
.0550	319.8				
.0670	760.0				

Desorption

Several experiments were made on desorption, which was found not to be entirely reversible. **A** certain amount of sulfur dioxide was found to remain in the gel in every case even after outgassing for several hours.

Calculations

From the weight taken up per gram of gel and the density[4] of sulfur dioxide the volume of liquid sulfur dioxide adsorbed was calculated. From the partial pressure of the sulfur dioxide for the various temperatures and the vapor pressure of liquid sulfur dioxide for the same temperature,[5] the corresponding pressures were calculated. Using values for the surface tension of liquid sulfur dioxide obtained by interpolation of Patrick[6] and Landolt and Börnstein,[7] the term $P\sigma/P_0$ was evaluated, which is used in Patrick's equations.[6] Curve I shows the results when log v is plotted against log $P\sigma/P_0$.

The adsorption affinity, E,[8] was calculated also and plotted against the volume adsorbed. Table II gives in Col. 1 the volume of sulfur

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[4] Landolt-Börnstein, "Chemical Tables," Vol. I, 285 (1923).

[5] Landolt-Börnstein, "Chemical Tables," Vol. II, 1349 (1923).

[6] McGavack and Patrick, THIS JOURNAL, 42,946 (1920).

[7] Landolt-Börnstein, "Chemical Tables," Vol. I, 242 (1923).

[8] **Polanyi,** *Verhandl.* deut. *Physik. Ges.,* 18, 55 (1916); Berenyi, *Z. physik. Chem.,* **94,** 62 (1920).

dioxide adsorbed by the gel, in Col. 2 the volume read from the curve representing the Polanyi Equation and in Col. **3** the percentage deviation of the former from the latter.

TABLE II

AGREEMENT OF OBSERVED VOLUMES ADSORBED WITH THOSE OBTAINED FROM POLANYI EQUATION

Vol. obs.	Vol. read from curve	Deviation, %	Vol. obs.	Vol. read from curve	Deviation, %
	−22.5° C.			25° C.	
0.0417	0.0426	2.11	0.0350	0.0350	..
.0507	.0502	0.99	.0363	.0370	2.16
.0625	.0620	0.80	.0390	.0382	2.09
.0640	.0670	4.47	.0420	.0410	2.38
.1055	.1035	1.93	.0476	.0460	3.48
.2110	.2110	..	.0510	.0500	2.00
			.0616	.0630	2.22
	50° C.			0° C.	
0.0197	0.0180	9.43	0.0372	0.0370	0.54
.0250	.0240	4.16	.0394	.0395	0.25
.0296	.0292	1.37	.0407	.0410	0.73
.0362	.0340	6.47	.0480	.0480	..
.0386	.0360	7.22	.0687	.0680	1.03
			.1200	.1175	2.13
			.1690	.1690	..

Discussion of Results

When the log of the weight of sulfur dioxide adsorbed per g. of gel is plotted against the log of the partial pressure of sulfur dioxide, the well known Freundlich isotherms are obtained.[9]

Our data show breaks in the isotherms corresponding to the theoretical curve of Coolidge.[10]

The breaks occur on the 0 and —22.5" curves, and at the same volume, as shown by the curve representing the Patrick formula. This is in accord with Patrick's views; however, the breaks occur at a relative pressure of 0.284—contrary to Patrick's Theory, which demands breaks at relative pressures of nearly 1.0. Nevertheless, the Patrick formula is an improvement over that of Freundlich, as it brings all the isotherms on one curve and holds over the same range as the Freundlich equation.

The curve obtained from our data is of the usual shape for the Polanyi Equation.[11]

It represents the data fairly well even in the region beyond the break in the Freundlich curves, with an accuracy that is comparable to that over the region before this.

[9] Freundlich, English Edition of "Capillary Chemistry," 1922, p. **115.**

[10] Coolidge, THIS JOURNAL, **48, 1798 (1926).**

[11] **Ref. 9, 1926, p. 123.**

Summary

Adsorption of sulfur dioxide by titania gel has been measured at −22.5, 0, 25 and 50°.

The data have been tested by the equations of Patrick and Polanyi and while the data substantiate Patrick's formula at lower relative pressure, over the whole range they can be best represented by the formula of Polanyi.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY AND FROM THE CRUFT LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES. I. AN EXPERIMENTAL AND THEORETICAL STUDY OF PRINCIPLES OF DESIGN OF THE WHEATSTONE BRIDGE FOR USE WITH ALTERNATING CURRENTS AND AN IMPROVED FORM OF DIRECT READING ALTERNATING CURRENT BRIDGE

BY GRINNELL JONES AND ROSWELL COLT JOSEPHS

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Introduction

It would be a pleasure to write an historical review of the previous work on the conductance of electrolytes with appreciative comments on the contributions of many earlier investigators including especially Kohlrausch, Wien, Noyes, Taylor and Acree, Grover and Curtis, Washburn, Kraus, Parker, Miller, Hall and Adams, Morgan and Lammert and many others, but the limitations of space firmly imposed by an Editor who must constantly remember his budget forbid. Moreover, such a review is unessential since the recent paper of Morgan and Lammert[1] contains an excellent summary of the earlier work.

Washburn[2] made substantial improvements in the design of the bridge

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[1] (a) J. Livingston R. Morgan and Olive M. Lammert, THIS JOURNAL, 48, 1220 (1926). In addition to the numerous papers referred to in this article the following will be of interest to students of this subject: (b) Wien, *Wied. Ann.*, 58, 37 (1896); (c) Miller, *Phys. Rev.*, [21 22, 622 (1923); (d) Reichinstein, *Z. Elektrochem.*, 15, 734, 913 (1909); (e) 16,916 (1910); (f) 17, 85, 699 (1911); (g) 19,384, 518 (1913); (h) Hall and Adams, THIS JOURNAL, 41,1515 (1919); (i) Randall and Scott, *ibid.*, 49,636 (1927).

[2] (a) Washburn, THIS JOURNAL, 38, 2431 (1916); (b) Washburn and Bell, *ibid.*, 35, 177 (1913); (c) Washburn and Karr Parker, *ibid.*, 39, 235 (1917). The senior author of this paper was a colleague of Professor Washburn at the University of Illinois while Washburn was engaged in the earlier part of his researches in this field and thus, although not sharing in these investigations directly, had the opportunity of following their progress in detail and acquired at first hand an appreciation of Washburn's important contributions to the measurement and interpretation of conductance of electrolytes. The researches to be described in this and subsequent papers were begun after

and conductivity cells which have been incorporated in the apparatus built by Leeds and Northrup. This apparatus,[3] which is the best commercially available, is now generally used, at least in the United States, for precision work. Therefore, in the following discussion of bridge design, emphasis will be placed on the defects of this apparatus and upon the changes in design we have found to be desirable.

In this paper is described an experimental and theoretical study of the design of the Wheatstone Bridge for measuring resistances with alternating current of audio frequencies 500 to 3000 cycles per second. Several sources of error, hitherto entirely overlooked or inadequately guarded against, have been found and means for their elimination invented. A new form of bridge which is more precise, sensitive and convenient than any hitherto available has been built, tested in service with satisfaction, and is described in detail. An experimental study of electrode effects and cell design is now in progress and will form the subject of the second paper in this series. A redetermination of the absolute value of the specific conductivity of certain standard solutions by a new method has been planned, and a beginning made in its execution.

In our preliminary study of the behavior of the Wheatstone bridge, we replaced the cell by a metallic resistance in order to avoid complications due to electrode phenomena. We planned to study these phenomena after errors in the bridge itself had been eliminated as much as possible. The apparatus was so constructed that each part could be replaced in turn by others of a different make or design and comparisons made by direct substitution or by interchange of the arms of the bridge. Capacitance could be introduced at will at any point and in any amount by means of variable electrostatic air condensers suitably connected. Various methods of grounding and shielding were tested. We had a double throw switch which permitted either the oscillator (giving controllable frequencies from 500 to 2400 cycles per second) or a direct current battery to be used as the source of the current. There was also a reversing switch in the line supplying power to the bridge. Another double throw switch substituted a direct current galvanometer for the telephone. We could thus detect any difference between the balance of the bridge with direct current and with alternating current of various frequencies, and thus seek out any

Washburn had turned his attention to other subjects and the senior author had left Illinois.

Before the publication by Morgan and Lammert of their second paper which announced their extensive program of investigation on the measurement of the conductance of solutions, we had made substantial progress on a similar program; but our methods were so different from theirs, as disclosed in their first and second papers, that we decided not to abandon our program in spite of the fact that they had an earlier start on the work.

[3] Leeds and Northrup Company, Philadelphia, Catalog No. 48.

abnormal behavior of the bridge or of any of its parts with alternating current due to capacitance, inductance, dielectric losses, improper grounding, shielding or other causes. These effects, although mostly small, were so numerous, subtle and concurrent that we made thousands of measurements in an effort to understand and locate the disturbances and devise remedies. We were endeavoring to avoid any imperfection of design, construction, or operation which might cause an error of 0.001%. This experimental study stimulated theoretical analysis of the sources of error. We have thus reached conclusions as to the correct principles of design which have guided the design and construction of the new bridge to be described below.

A detailed record of these numerous experiments is inadvisable because of their great number, and because the actual numerical data are significant only in regard to particular pieces of apparatus. In many cases, especially in the earlier part of the work, the interpretation of the experiments was greatly complicated by the fact that several sources of error were superimposed on one another. For the sake of brevity and clearness the following discussion is mainly theoretical, with selections from our experimental data used for illustrative purposes, but our method of approach was primarily experimental. Every source of error which is discussed was first found experimentally in apparatus of supposedly good quality and has been shown experimentally to be significant in work of high precision with the forms of apparatus commonly used by investigators who are striving for accuracy.

The Source of Alternating Current

Taylor and Acree[4] have used and recommended the Vreeland Oscillator as a source of alternating current, and have demonstrated that it is superior to other forms of oscillators previously used. Recently Morgan and Lammert have made a careful study of the instrument and have shown that its frequency is not constant when used steadily over long periods hut varies by about 1% in the course of several hours' operation. They ascribe this variation to a change in capacitance and inductance due to heating; but as is explained below we do not regard this variation in frequency as a serious fault. This instrument, being supplied as a part of the Leeds and Northrup set, has been most used in precision work in recent years. But the Vreeland Oscillator has many disadvantages. It is expensive in first cost ($225) and in operation. It uses 5 amperes at 110 volts D.C. and therefore requires either a large storage battery or a motor generator to operate it. Its efficiency is very low, as only a small part of this energy is actually supplied to the bridge or needed by the bridge. In the standard form available by purchase it gives an unneces-

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[4] Taylor and Acree, THIS JOURNAL, 38, 2396 (1916).

sarily high voltage which tends to overheat the cell unless the bridge is protected by a high resistance in series or by shunts. This fault is, however, not inherent, as the coils can be wound to give any desired voltage. It has a strong variable magnetic field which produces serious disturbances by inducing currents in the bridge and telephone unless the oscillator is placed at a considerable distance. When operated by a motor generator it often gives erratic rasping noises due to sparks at the commutator of the dynamo. It has a tendency to stop oscillating in the midst of the readings and can then only be started by tipping it by hand, which is a nuisance because the instrument must be located at a considerable distance.

Hall and Adams[5] have suggested the use of the three electrode or triode tube sometimes called an audion tube, suitably connected with inductance and capacitance so that it oscillates. Although the chemical literature gives little indication that such instruments have been used by chemists, audion tube oscillators are now used as a matter of course in radio research laboratories. Splendid instruments of this type may now be purchased.[6]

We give in Fig. 1 a schematic wiring diagram of a simpler and cheaper oscillator which we have used with great satisfaction, although no special merit is claimed for the details of the design. Switches S_1 and S_2 permit four different values of the capacitance and four different values of the inductance to be used in the oscillating circuit so that sixteen different frequencies can be obtained between the limits of 500 and 2400 cycles. We have ordinarily used 1100 and 2400 cycles. It could easily be modified to give frequencies up to 5000 cycles if it were desired. The three coils are mounted on the same axis. By moving the output coil on this axis the voltage supplied to the bridge can be varied in at least a fourfold ratio. The voltage can also be varied in about a 4 to 1 ratio by moving the switch, S_3, which controls the number of turns used in the output coil. By the combination of these two methods the voltage can be varied 16-fold. The maximum voltage of the output coil of this oscillator is about 5 volts. The output coil O, has a grounded electrostatic shield consisting of a wire wound as an open toroid around it in three independent sections, each connected to ground at one end. This shielding of the output coil is the only unusual feature in the design and is of considerable importance for the reason explained below (page 1060).

The audion tube oscillator has several important advantages over the Vreeland Oscillator.

1. It is much cheaper to build and operate. Our instrument was made of standard radio parts and cost only $60 including all parts and the labor of an experienced builder of radio sets. This cost is, however, not fairly comparable with the prices of purchaseable oscillators mentioned

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[5] (a) Hall and Adams, THIS JOURNAL, 41, 1515 (1919). See also (b) Randall and Vanselow, *ibid.*, **46**, 2424 (1924); (c) Randall and Scott, *ibid.*, **49**, 636 (1927).

[6] Bulletin 803 of the General Radio Company of Cambridge, Mass., describes their type 377 Low Frequency Oscillator having a range from 60 to 75,000 cycles and listed at $375. The Western Electric Company also makes an instrument having a range from 100 to 50,000 cycles which is sold for $1750. These instruments have greater power and a greater range of adjustment in voltage and frequency than we have found necessary for our purposes.

above as it does not include any overhead, or selling expenses. It can be operated with a six volt "A" storage battery and a sixty-seven volt "B" dry battery.

2. It is easily adjustable in frequency and voltage within any limits that may be needed and can be designed to give any desired number of steps in frequency.

3. Its outside magnetic field is much less than that of the Vreeland Oscillator.

4. It can be started and stopped conveniently and instantly by a switch in the "A" battery line and never stops of its own accord when in use.

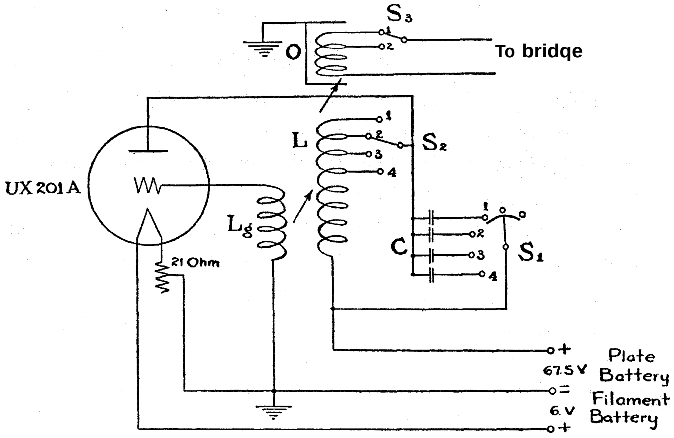

Fig. 1.—L=oscillating coil: 4 in. inside diameter, $6^3/_8$ in. outside diameter. 1 in. length, No. 21 double cotton covered, 760 turns, taps at 650, 520, 475 turns; L_g=grid coil: 5 in. inside diameter, $6^1/_4$ in. outside diameter, $^3/_8$ in. length, No. 30 double cotton covered, 540 turns; O=output coil: $3^3/_4$ in. inside diameter, $4^1/_4$ in. outside diameter, $^1/_4$ in. length, No. 30 double cotton covered, 140 turns, tap at 35 turns, shielded; C=condenser: three, 0.1 p f. and one, 1.0 p f. paper condenser, capacitance for successive positions 1–.1 μ f., 2–.2 μ f., 3–.3 μ f., 4–1.2 μ f.

Our instrument has two slight defects which are, however, not serious and can be cured by methods well known to radio engineers but which we have not yet adopted because they did not seem worth the trouble and expense involved. Our instrument has a harmonic of very low intensity. barely audible with a two stage amplifier when the primary note is balanced out perfectly. It could be removed by suitable electrical tuning if it were troublesome. The other defect is that the frequency changes slightly with changes in the load, but this has not proved to be of any consequence in any work which we have as yet done with our bridge because our bridge is so designed that the load varies only slightly in use and, as we shall show in the second paper of this series, even relatively great changes in frequency (from 1100 to 2400) have only a very slight effect on the bridge setting, unless the conditions are such that excessive polarization occurs, or unless other sources of error which are functions of the frequency are present. Therefore, a change of frequency of a few per cent. is of no consequence. If it is desired to make the frequency entirely independent of the resistance being measured, this could be done by using two audion tubes, one of which oscillates at a fixed frequency, while the other acts as an amplifier and takes all the variation in the load without influencing the oscillating tube. However, the use of an amplifier in this way may add a weak second harmonic which can be tuned out by the method indicated above.

The Telephone and Amplifier

According to Washburn's analysis of bridge design the .controlling factor of many features of the design, especially of the cells, is the sensitiveness of the telephone.[7] Hall and Adams[5a] have suggested the use of an audion tube amplifier with the telephone, which makes it possible to increase the sensitiveness of the detector as much as may be desired. They point out that this device makes it possible to reduce substantially the current in the bridge proper, thus minimizing the heating effect and polarization in the cell, which aids greatly in precision work; at the same time it increases the sensitiveness of the bridge setting and avoids the nervous strain of listening to very weak notes in the telephone. Our experience fully confirms these advantages. We have secured a sensitiveness of one part per million in the bridge setting. On one occasion we have used two stages of amplification with a loud speaker so that the balancing of the bridge could be heard by an audience in a lecture room. Ordinarily we use telephones with one or two stages of amplification. According to Washburn's analysis, which is in accord with our experience with his apparatus, the resistance of the cell should be between 200 and 10,000 ohms for precision measurements. Hall and Adams were successful with the amplifier in extending this limit downward to about 100 ohms but they were not interested in increasing the range in the other direction and record no experiments with cells of high resistance. For our purpose it was desirable to use cells of much higher resistance. By the use of the amplifier and of other improvements to be described below we have obtained sharp settings of the bridge with a cell having a resistance of 60,000 ohms and an approximate setting with a cell having 1,500,000 ohms. The use of high resistances and very small currents minimizes errors due to heating and polarization or other electrode effects and permits the design of a cell as a long narrow tube which gives better thermal contact with the liquid in the thermostat. The latter is of considerable

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[7] Washburn, ref. 2 a. See especially p. 2442.

importance since temperature control is expected to be the largest source of error in our final measurements. The amplifier also makes it unnecessary and undesirable to tune the telephone for maximum sensitiveness at some particular frequency with a sacrifice of sensitiveness at other frequencies.

Mathematical Theory of the Wheatstone **Bridge** for Alternating Currents

Fig. 2 is a diagrammatic representation of the Wheatstone Bridge for use in measuring the resistance of the cell H with alternating current supplied by the oscillator O. (The oscillator could be replaced by a battery by means of a switch not shown in Fig. 2 but shown in Fig. 8.) The current detector consists of a telephone or an amplifier and a telephone. (When using direct current the telephone could be replaced by a galvanometer by means of a switch not shown in Fig. 2 but shown in Fig. 8.)

The electrolytic cell, H, whose resistance is to be measured is assumed to be in branch 2 of the bridge circuit. The cell unavoidably has some reactance due to its geometrical capacitance or to polarization. Branch 1 consists of a variable resistance box and a variable air condenser in parallel. It will be proved below that this arrangement is the best to compensate for the capacitance of the cell, which is necessary to obtain a precise measurement of the resistance. Branches 3 and 4 are the ratio arms. Subscripts 1, 2, 3, 4, are used to designate the several branches. E_1 is the effective or virtual potential difference across Branch 1 (between A and B'). I_1 is the virtual or effective current in Branch 1.

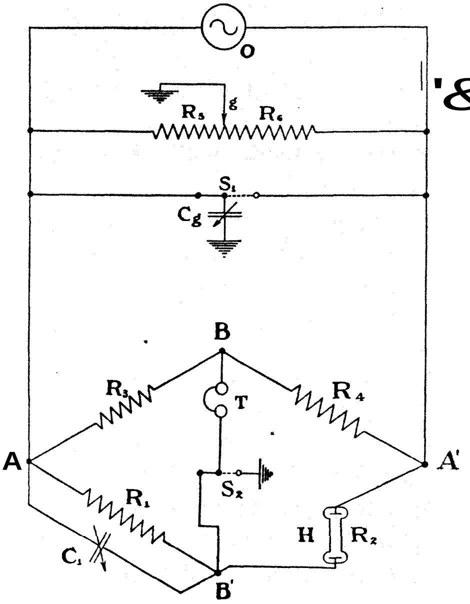

Fig. 2—Schematic wiring diagram *of* bridge showing new method *of* grounding.

Both E and **I** are harmonic functions of the time, but the maximum current and the maximum voltage may not occur **at** the same instant of time, in which case they are said to be out of phase and are to be treated in the conventional manner as vectors. In a strict sense of the term the voltage and current are not vectors because the difference in phase is not a difference in direction but a difference in time. But in the simplest form of alternating current generator—a single loop of wire revolving at constant angular velocity on an axis at right angles to a uniform and a steady magnetic field--one complete revolution of the loop generates one cycle. Therefore, differences in time are exactly correlated to differences in direction of the loop. This makes it possible to treat the phase relationships by mathematical methods applicable to vectors. One complete cycle corresponds to 2π radians or 360° and fractions of a cycle may be expressed in circular degrees.

R_1 is the equivalent series resistance of branch 1. In other words, R_1 is that perfect resistance which when placed in series with a perfect condenser of suitable size would be electrically equivalent to the imperfect resistance actually used when shunted by the imperfect condenser actually used. R_1 is not necessarily the same (unless suitable precautions are taken) as the direct current resistance of the box, since there may be dielectric losses in the resistance box or in the condenser, or other causes for a difference between the direct current resistance and the alternating current resistance.

X_1 is the equivalent series reactance in this branch. It may in theory be due either to inductance or to capacitance or to both. Except in unusual cases, the capacitance predominates. This reactance is due to the condenser and to any capacitance and inductance in the box and connections.

Z_1 is the impedance in the branch AB', whose magnitude may be computed from the equation $Z_1^2 = R_1^2 + X_1^2$, but this procedure loses sight of the phase relationships. For this purpose it is better to use the conventional symbolism of vectors, $Z_1 = R_1 + jX_1$, where the equality sign signifies geometrical addition of the vectors, R_1 and X_1 and the symbol j means that R_1 and X_1 are to be treated as vectors at right angles to each other. R is commonly plotted horizontally and X vertically so that the resistance is often spoken of as the horizontal component of the impedance and the reactance as the vertical component of the impedance.[8]

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[8] Some authors speak of R as the real component and X as the imaginary component of the impedance. This usage is confusing because both R and X are real in the sense that they are definite functions of the dimensions of an electrical circuit (or part of a circuit) and of the frequency and have a definite effect on an electrical current. This use of the term imaginary has its origin in the practice of many mathematicians in calling $\sqrt{-1}$ an imaginary quantity. This is poor pedagogy, which has caused unnecessary confusion in the minds of many defenseless students. Let j be the symbol of the operation of rotating a vector through 90° counterclockwise. If a in Fig. 3 represents a vector having magnitude and direction, then ja represents another vector having the same magnitude but a direction at right angles to a, and j^2a would represent the vector obtained by the rotation of a through two right angles, which would

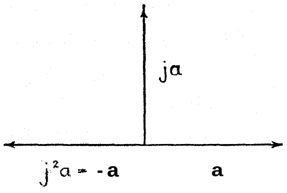

Fig. 3.

According to Ohm's law as applied to alternating current, $E_1 = I_1Z_1 = I_1(R_1 + jX_1)$ (not $E_1 = I_1R_1$ unless $X_1 = 0$ and hence $R_1 = Z_1$ which, in general, is not true).

Branch 2 from B′ to A′ is assumed to contain the cell H which contains the solution whose resistance is to be measured. This cell will act like a resistance R_2 in series with a condenser which gives a reactance X_2 and as before we can write $E_2 = I_2Z_2 = I_2(R_2 + jX_2)$. R_2 is not necessarily the same as the true electrolytic resistance of the solution inside the cell plus the resistance of the electrodes and lead wires, because there may be an irreversible dissipation of energy by other means than the passage of a current through a pure resistance which will influence the measured resistance. These possible sources of error will be studied in detail in the second part of this investigation.

Similarly, X_2 is the reactance which is the combined effect of the inductance and capacitance in this arm together with the reactance due to all other processes which convert electrical energy reversibly, and change the phase relationships of the voltage and current. An example of the latter is reversible polarization. During alternating current electrolysis electrical energy is converted into chemical energy at the electrodes during one half of the cycle and returned to the system as electrical energy during the other half cycle. This process is of the nature of capacitance in that it causes the current to lead the voltage but the reactance due to polarization may not vary with the frequency in the same manner that it does for a geometrical capacity and may be a function of the voltage instead of being independent of the voltage as it is for a geometrical capacity. Therefore, R_2 represents that pure resistance which would dissipate the same amount of electrical energy that is dissipated by all of the other processes in arm 2 under the given conditions of frequency; and X_2 is that pure reactance in series with R_2 which would cause the same phase change. It must be kept in mind, however, that the energy-dissipating and the phase-changing effect of polarization may not be equivalent to any actual combination of pure resistance and pure reactance. $Z_2 = R_2 + jX_2$ and $E_2 = I_2Z_2 = I_2(R_2 + jX_2)$.

Branch 3 (from A to B) and Branch 4 (from B to A′) are the ratio arms of the bridge, which may be either fixed and equal, or variable resistances, R_3 and R_4, but which are variable in the Leeds and Northrup apparatus. In our final apparatus R_3 and R_4 are made fixed and equal, which gives important advantages, as will be pointed out more in detail below. Unless unusual precautions are taken the inductances and capaci-

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be represented by $-a$; therefore $j^2 = -1$, or $j = \sqrt{-1}$. But j or $\sqrt{-1}$ is not imaginary, but is a mathematical operator which has a very definite and clear meaning—rotation through a right angle. Steinmetz, "Engineering Mathematics," McGraw-Hill Book Company, New York, 1911, pp. 13–16.

tances in these resistances will not be negligible and therefore we must ascribe reactances, X_3 and X_4, and impedances, Z_3 and Z_4, to these arms also. We may, therefore, write $E_3 = I_3Z_3 = I_3(R_3 + jX_3)$; and $E_4 = I_4Z_4 = I_4(R_4 + jX_4)$.

When the bridge is balanced so that no current flows through the telephone, the potential at B must be equal to the potential at B' at every instant; or, in other words, the potential must be in phase, as well as have the same numerical value; then $E_1 = E_3$ and $E_2 = E_4$. Therefore we may write

$$\frac{I_1Z_1}{I_2Z_2} = \frac{I_3Z_3}{I_4Z_4} \tag{1}$$

and, moreover, *if there is no escape of current from the bridge network by ground connections or through capacitance to ground or through capacitance to any other conductor and if there is no mutual capacitance or mutual inductance between the arms and if there is no leakage* from any part of the bridge to any other part or to the ground or to any outside conductors, then $I_1 = I_2$ and $I_3 = I_4$ and hence

$$\frac{Z_1}{Z_2} = \frac{Z_3}{Z_4} \tag{2}$$

It is apparent from this analysis that there is a fallacy in the method of grounding incorporated in the Leeds and Northrup apparatus, which consists in making a direct connection to ground from the midpoint of the bridge at B^1. Such a ground connection makes it easier to secure silence in the telephone, as may easily be verified by trial. But this ground connection can only be effective by leading current to earth and then $I_1 \neq I_2$ and therefore $Z_1/Z_2 \neq 23/24$. Therefore, a ground connection at the mid-point of the bridge is inadmissible.

A New Method of Grounding the Bridge

There is, unavoidably, considerable capacitance between the telephone coils and the observer (who may or may not be grounded) or between the primary and secondary coils of the transformer if an amplifier is used. The best way to avoid a charging current into this capacitance, which would upset the proper balance of the bridge and prevent a sharp minimum, is to maintain both the observer and the telephone (when in balance) at earth potential. As a substitute for the method of grounding at the mid-point of the bridge we first tried the method used by Taylor and Acree,[4] which consists of a high resistance shunted across the bridge and grounded at its mid-point. This method is described by Taylor and Acree as a modification of that used by Wagner.[9] But a study of Wagner's article shows that his grounding is essentially different, inasmuch as Wagner was using a capacity bridge and had resistance and capacitance in series in his shunt, with the ground connection between the resistance

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[9] *Wagner, Elektrotechnische Zeitschrift*, 32, 1001 (1911).

and capacitance, while Taylor and Acree used no condenser in their ground connection. This method was found to be unsatisfactory, but before explaining our solution of the problem it will be well to discuss another source of error which turned out to be related to the grounding and also curable by proper grounding.

In order to avoid errors due to thermo-electric forces when using direct current in our bridge we had a reversing switch (not shown in Fig. 2, but shown in Fig. 8) in the battery line between the bridge and the switch which controlled the kind of current used. We then noticed that when using alternating current and a Taylor and Acree ground the reading of the bridge when in balance depended upon the position of the reversing switch which was near the bridge. The observation that merely reversing the lead wires which supplied power to the ends of an alternating current bridge could change the reading of the bridge was astonishing in view of the fact that the current was automatically reversing itself one thousand times per second. We have found no record that this phenomenon had been observed before by anyone using an alternating current bridge to measure electrolytic or metallic resistances; but after making this observation we found that Wagner had made a similar observation when using a capacity bridge. After many experiments of a varied character we finally traced the cause to an unbalanced or unsymmetrical capacitance from the oscillator and its lead wires to earth. We connected one side of a variable air condenser to each lead wire from the oscillator at the terminal of the reversing switch nearest the oscillator and connected the other side of each condenser to ground. We then found that by putting the proper amount of capacitance in one or the other of the condensers the reading of the bridge when in balance became independent of the position of the reversing switch. We also found that the definite reading thus obtained was the mean of the two divergent readings previously obtained when the position of the reversing switch was changed, and also the same as the reading with direct current when all other sources of error were eliminated. Then by connecting capacitance to the other lead wire the effect of the reversing switch could be magnified. Errors of one-tenth of one per cent. in the bridge reading can be easily obtained in this way. Apparently an inequality in the capacitance to earth from the two lead wires or an unsymmetrical capacitance between the oscillator and earth causes an error in the setting.

This effect can best be made clear by an example chosen from a great many in our notebooks. In this particular case the bridge was grounded at its midpoint and when balanced with an alternating current gave a result differing by +0.030% from the balance with direct current. Then on reversing the lead wires from the oscillator the new balance was in error by —0.031%. After replacing this ground connection with a ground similar to that used by Taylor and Acree the error was plus or minus 0.025% according to the position of the reversing switch. Then on connecting a condenser of about 1000 micromicrofarads from one lead wire to earth the error was reduced to ±0.006%. By increasing the capacitance between the lead wire and earth to 2000 micromicrofarads the error was reduced to 0.000% as compared with the direct current reading and the position of the reversing switch no longer had any effect on the reading. There was evidently in this case an asymmetry of 2000 micromicrofarads between the ground and the two lead wires, which caused the trouble.

We then rebuilt our oscillator and leads with a special effort to make the capacity to earth as small, fixed and symmetrical as possible. A grounded electrostatic shield was placed around the output coil of the oscillator. We found that with no ground at all on the bridge the error was ±0.045% according to the position of the reversing switch. With the mid-point grounded or with the Taylor and Acree ground the error was reduced to ±0.002%. This was a substantial improvement over the results obtained before the reconstruction of the oscillator. Moreover, it was now found that only 20 micromicrofarads were needed to bring the effect of reversing the switch to zero. After many experiments we reached the conclusion that the actual amount of the capacitance to earth from the lead wires and oscillator is relatively unimportant provided that this capacitance is made as definite as possible by mounting the lead wires in a fixed position inside a grounded metallic sheath and provided that the capacitance from the two wires to earth is adjusted to equality by means of a condenser until the effect of reversing the switch disappears. Some experiments with a Vreeland Oscillator showed that this effect is also present. The discovery of this source of error throws some suspicion on all previous measurements of the conductance of solutions. This effect is also a function of the frequency and may perhaps account for the apparent change in conductance with frequency which has been reported by several investigators. This is a matter which we expect to investigate carefully with our new and improved bridge.

We have devised a method of grounding which cures the reversing switch effect and also maintains the telephone when in balance at earth potential, which is necessary for the reasons pointed out above, without making a direct connection between the bridge and earth as is customarily done. Our method of grounding is a modification of the method suggested by Wagner.[9] Wagner was working with a capacity bridge, so that his scheme cannot be used for a resistance bridge just as he described it, but the fundamental idea is adaptable to the resistance bridge.

The modified form of the Wagner ground which we have used successfully is shown in Fig. 2. It consists of an auxiliary resistance, AR_5R_6A', in parallel with the bridge proper, provided with a sliding contact, g, which is connected to earth, and a variable air condenser, Cg, one side of which is connected to earth and the other side connected through a switch, S_1, to either A or A' whichever may prove to be necessary. The sliding contact divides the auxiliary resistance into two parts, R_5 and R_6, and can be adjusted so as to make R_5/R_6 approximately equal to R_3/R_4.

The procedure in adjusting this ground is:

1. Make an approximate adjustment of the bridge proper (R_1 and C_1), leaving the ground as it happens to be from the last use.

2. By means of a suitable switch, S_2, disconnect the telephone from B' and connect this lead wire to earth instead, while the other side of the telephone remains connected to B.

3. Adjust the sliding contact, g, and the variable condenser, Cg (in magnitude and position across R_5 or R_6), until there is silence in the telephone, thus bringing B to earth potential.

4. Throw the switch, S_2, so that it restores the telephone to its original position from B to B' and breaks the connection between the telephone and earth.

5. Adjust the bridge (R_1 and C_1) again. If this second adjustment is much different from the original, the adjustment of the ground should be repeated and then the final bridge reading confirmed. In our experience the capacitance adjustment in the grounding device is even more important than the resistance adjustment. With suitable switches built into the apparatus this adjustment of the ground requires only a few seconds for an experienced operator. This arrangement and procedure ensure that B and B′ are at earth potential, accomplishing it in a manner that cannot upset the equality of I_1 and I_2, and of I_3 and I_4.

Wagner had an auxiliary line shunted across the ends of his bridge, consisting of a variable resistance and a variable capacitance in series with the ground connection between the two. In his arrangement the impedance in arm 5 was due wholly to resistance and the impedance in arm 6 was due wholly to capacitance. In a resistance bridge the condenser is most advantageously placed in parallel with either R_5 or R_6 as may be found by trial to be needed so that the impedance in one of these arms is due partly to resistance and partly to capacitance. This is the difference between our arrangement of the ground and Wagner's. The magnitude of R_5 and R_6 should be approximately the same as R_3 and R_4. This method of grounding brings the telephone when in balance to earth potential so that it only remains to ensure that the head of the observer which is near but insulated from the wires in the telephone is also at earth potential. This can be accomplished simply and in a manner which cannot be forgotten by covering the hard rubber of the telephone ear pieces with tin foil which is permanently connected to earth by means of an auxiliary wire mechanically attached to but electrically insulated from the telephone lead wires.

The essential difference between our method and that of Taylor and Acree is that they used no variable condenser, Cg, and their earth connection was fixed rather than sliding so that $R_5 = R_6$ but, since Taylor and Acree were working with an equal arm bridge with R_3 always equal to R_4, an adjustment of R_5 and R_6 was relatively unimportant, although we have found that even with an equal arm bridge some adjustment of R_5 and R_6 is helpful. It is our experience that the proper adjustment of the capacitance is the most important part of the ground connection, although without a test on their apparatus it is impossible to judge how important it may have been in their experiments.

Morgan and Lammert[10] state, "The method of grounding which we have found most effective is the modified form of Wagner described by Taylor and Acree. By this method each end of the bridge is grounded through a 1000-ohm resistance and the lead wires from the oscillator shielded and grounded. We cannot emphasize too much the need for a good ground in order to get a sharp minimum. With the set-up described there is probably nothing which so affects the sharpness of the minimum as the condition of the ground." Evidently Morgan and Lammert, like Taylor and Acree, have no adjustable condenser in their ground connection and therefore no provision for a reactance balance in their modification of the Wagner ground. In Morgan and Lammert's arrangement R_5 and R_6 are maintained constant at 1000 ohms, although in their bridge R_3 and R_4 are variable and therefore for the best results R_5 and R_6 should be capable of corresponding adjustment. In this respect their arrangement is inferior to that of Taylor and Acree, but if in practice R_3 and R_4 are always nearly equal this is less important than the omission of the variable condenser. We agree with Morgan and Lammert as to the importance of a "good ground," but we believe that the resistance in the ground connection is of minor importance compared to having it built in accordance with the principles explained above.

Magnetic Shielding

Care should be taken to make sure that there are no variable magnetic fields in the space occupied by the bridge which might cause an error by inducing a current in the bridge. A sensitive and convenient way to search for variable electromagnetic fields is to take a coil of wire (about 50 turns with a six inch diameter), attach the ends of the coil to a telephone (with or without an amplifier) and hold the coil in various positions near the bridge, taking care to turn it frequently. If a noise is heard in the telephone this proves that there are variable magnetic

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[10] Morgan and Lammert, THIS JOURNAL, 48, 1232 (1926).

fields which may cause error by inducing currents in the bridge circuit. By noticing the pitch of the note heard, the direction of the field and the effect of starting and stopping various electrical machines in the neighborhood the source of the disturbance can be located. The disturbance may come from the oscillator or any near-by electric motor. The bridge itself if properly designed has so little inductance that it is far less sensitive than the testing coil which has been suggested and is not appreciably affected by outside electromagentic fields; but the coils in the telephone itself are sensitive to varying magnetic fields and if an audion tube amplifier is used the trouble is more serious because the coils in the transformers may have alternating currents induced in them which are amplified.

An effective electromagnetic shield requires several concentric enclosures in heavy iron and it is therefore impractical to shield the bridge or telephones, but the amplifier can be shielded. **A** better remedy is to make the oscillator as nearly **as** possible astatic (this is not possible with the Vreeland oscillator, which is a particularly bad offender), enclose it in one or more iron shields, such as an iron barrel, and finally and most important and easy, remove it to a considerable distance. We have found it necessary to remove the Vreeland oscillator to a distance of thirty feet, whereas with our form of audion tube oscillator ten feet is ample. If near-by motors are unavoidable they may be stopped momentarily while the final readings are being taken.

Electrostatic Shielding

It is a common practice to place a grounded metallic shield between the parts of the bridge proper[11] or to surround the bridge completely by a grounded shield for the purpose of preventing electrostatic influence on the bridge from the outside. It is our judgment, based on reasoning and experiment, that this practice is apt to cause more error than it cures. In the derivation of the fundamental equation for the bridge it is assumed that there is no escape of current from the bridge to ground and no transfer of electric energy between the four arms through any other means than conduction at the junction points of the arms. Therefore, by reasoning analogous to that used above to prove the fallacy of grounding the midpoint of the bridge, it becomes evident that the bridge must be so constructed and mounted that there is no appreciable capacitance between any of the four arms of the bridge proper to any other conductor, including the other three arms, the line supplying power to the bridge, the telephone leads or any other surrounding object such as the thermostat, the observer, the oscillator, electric light lines or the earth itself. If there is capacitance between arms 1 and 3, for instance, the proper remedy is to spread them

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[11] See, for instance, Leeds and Northrup Catalog No. 48, 1924, p. 3, Fig. 1. Numerous investigators have described more or less complete shielding of their bridges.

further apart. To put a grounded metallic plate between these arms does, in a certain sense, prevent direct exchange of energy between these arms, but it introduces a much larger capacitance between each of these arms and the earth, so that the effective indirect exchange of energy is increased and the error magnified. To put a grounded shield around the entire bridge will protect it from outside electrostatic influence but care should be taken that the shield is so far away from the bridge that the capacitance between the bridge and the shield is negligible. Such a shield is a nuisance in operating the bridge. It is better to put the shield around the outside source of disturbance if the disturbance cannot be removed to such a distance as to make it negligible.

The outside electrostatic influence most likely to disturb the bridge is the oscillator itself (this is true particularly of the Vreeland oscillator) because this disturbance is at the frequency used in the bridge and is sure to be operating when readings are to be taken. The best way to avoid this difficulty is to put the oscillator so far away that it is harmless, or to place a shield around the oscillator. A grounded enclosure of thin metal is an effective electrostatic shield. If an amplifier is used a sixty-cycle hum may be heard from electric light lines even at considerable distances. With practice it is possible to ignore this sixty-cycle note and make the balance with the comparatively high note given by the oscillator but it is better to have a double-pole pull switch at considerable distance operated by a cord so that the sixty-cycle line can be entirely disconnected momentarily when readings are to be taken. The lead wires from the oscillator must of course approach the bridge proper but these wires should be themselves shielded to within 15 cm. of the bridge for the reason explained above in the discussion of the grounding. Since these lead wires are at the same potential as the adjacent arms of the bridge they can do no harm provided the resistances through which the fall of potential in the arm occurs are placed far enough away from the junction point. The shield around the lead wires should be removed where it approaches the bridge because this would bring a grounded conductor too near the bridge.

We have tested this question experimentally by using a metallic plate 15 cm. square connected by a flexible wire either to earth, so that it would have zero potential, or to one end of the bridge, so that it would have the maximum potential of any part of the bridge, and then observed the effect on the bridge balance of moving the plate near to the various parts of the bridge. It was definitely proved that errors can be produced in this way although they are small. Even under extremely bad conditions we were only able to produce an error of 5 parts in 100,000 at 1100 cycles. The effect is of course greater at higher frequencies. From numerous experiments with this plate we inferred that 15cm. separation, with air as the medium, for parts having the maximum difference of potential is-sufficient to ensure that the error will be less than 0.001% with a frequency not greater than 2400 cycles. The line from bridge to the amplifier should be shielded because this line is at ground potential when the bridge is in balance and very nearly zero when the bridge is slightly out of balance, and therefore capacitance to earth can do no harm and this line is especially sensitive to outside electrostatic influence if an amplifier is used. The net result of these experiments on shielding was the conclusion that this is a comparatively unimportant source of error.

Water vs. Oil in the Thermostats

Most investigators have immersed their cells in thermostats filled with water and many have grounded the thermostat also. It is easier to maintain a constant temperature in a thermostat filled with water than with any other liquid because water has a high specific heat, a low viscosity which facilitates stirring and its slow evaporation dissipates surplus heat. Moreover, water is cheap, clean and odorless. But for electrical purposes water has the great drawback that it is a conductor. From the theory of alternating currents it may be inferred that the presence of a conductor so near the cell may cause an error in the measurement of the resistance due to the following causes.

1. The presence of the grounded conductor near one arm of the bridge causes bridge errors whose existence has been demonstrated by the experiments described above. The capacitance introduced by the grounded conducting liquid in the thermostat would be expected from purely geometrical considerations to be greater than the capacitance introduced by the metal plate in these experiments.

2. The walls of the glass cell may act as a dielectric in a condenser, permitting alternating current to flow in the water outside the cell. This extra parallel path for the current consisting of two condensers and a resistance must decrease the measured resistance of the cell. For convenience this may be referred to as the error due to capacitance by-path.

3. The alternating current in the cell will induce eddy currents in the water outside the cell and thus have the effect of increasing the apparent resistance in accordance with the well-known behavior of a short-circuited transformer. The eddy currents tend to counteract the error due to capacitance by-path.

4. The possibility of error due to skin effect in the relatively wide conductor inside the cell was considered but proved to be negligible by calculation in accordance with the well-known formula.

The above sources of error may be functions of the frequency, the resistance of the solution inside the cell, the specific conductivity of the water outside the cell, the dimensions of the cell and electrodes and proximity of the leads and the thickness and electrical properties of the glass used in making the cells, and the position of the cell with reference to the tub. The theoretical analysis of these three superimposed effects would be a problem of extreme mathematical difficulty which we have not attempted in detail. We have preferred an experimental attack on the problem.

In order to determine whether these errors are large enough to be significant we cleansed our thermostat and filled it with water of specific conductivity of 14×10^{-6}. Six conductivity cells of the pipet type, with cell constants ranging from 0.5 to 145, were filled with potassium chloride solution of a concentration suitable to give a high resistance (21,000-25,700 ohms) and then the resistance of each cell was measured with 1100 cycles and with 2400 cycles, with the metal thermostat tub grounded, and also ungrounded. Then a small amount of potassium chloride was added to the water in the thermostat sufficient to make it about 0.0002 *N* and to give a specific conductivity of 26×10^{-6} and the measurements were repeated. A further quantity of potassium chloride was then added to give a specific conductivity of 325×10^{-6} and a concentration of about 0.0025 *N*, and the measurements repeated. Then the water was removed and replaced with a good grade of transformer oil consisting of a refined petroleum distillate of a boiling point high enough to avoid offensive odor (Transil Oil) and the measurements were then repeated. With oil in the thermostat the measured resistances were absolutely independent of whether the tub was grounded or not, as was to be expected since the oil was a very good insulator. The results with oil in the tub were also independent of the frequency within at least 0.01% except in the two cells of the lowest cell constant (G and J) in which the so-called "electrode phenomena" were present.

The following table gives the results of these measurements. The figures are the difference between the resistance of the cell when immersed in water and in oil, expressed in per cent. A plus sign means that the resistance in water is the higher. These measurements were made with our new bridge to be described in detail below.

TABLE I

COMPARISON OF OIL AND WATER AS THERMOSTAT LIQUIDS

Cell designation		A	B	C	D	G	J
Approximate cell constant		144.6	51.5	45	9	3.05	0.515
In oil, ohms at 2400 cycles		21,755	21,364	24,118	25,694	24,311	21,071
In oil, ohms at 1100 cycles		21,756	21,363	24,117	25,694	24,314	21,076
Thermostat grounded							
Prequency	**Sp. cond. of water**	**Resistance in water − resistance in oil, %**					
2400	0.000014	+0.15	+0.18	+0.23	+0.17		
2400	.000026	.10	.11	.14	.10		
2400	.000325	.03	.02	.03	.02	+0.28	+0.12
1100	.000014	.05	.05	.07	.05		
1100	.000026	.04	.02	.04	.03		
1100	.000325	.01	.01	.01	.01	.24	.10
Thermostat not grounded							
2400	.000014	− .28	− .22	− .51	− .20		
2400	.000026	− .22	− .20	− .47	− .18		
2400	.000325	− .16	− .16	− .28	− .15	− .09	− .34
1100	.000014	− .11	− .09	− .22	− .07		
1100	.000325	− .08	− .07	− .15	− .06	+ .08	− .15

A consideration of these data confirms the theoretical prediction as to the complex character of the phenomena. In view of the almost universal neglect of this source of error by earlier investigators the magnitude of the error is surprising and disconcerting. The errors rise to 0.51% in the extreme case and errors of more than 0.1% are numerous. Other similar experiments which are not published in detail indicate that the errors increase with the increase of resistance being measured. This may be largely responsible for the difficulty found by many experimenters in the past in obtaining concordant results with high resistances, which has forced most experimenters to design their cells so as to give moderate resistances. These errors are appreciable in most cases even with the resistance in the cell as low as 300 ohms.

The error due to grounding the thermostat seems to be the most important. The effect of grounding was increased by moving the cell near the walls of the tub. In all of our measurements the effect of grounding the thermostat was to increase the apparent resistance. The error due to the capacitance by-path seems to take second rank in most cases. The error also varies from cell to cell but the correlation of these variations with the geometry of the cell is not clear. The large errors with cell C which is intermediate in its design are puzzling.

A quantitative interpretation of these data is beyond our powers at present and there are many anomalies for which a clear explanation is lacking. Interchanging the lead wires to the cell in some cases had a marked influence on the error. The grounding of the tub also had a marked influence upon the necessary adjustment in the grounding of the bridge and upon the reactance balance in the bridge proper.

But since we have a single remedy for all three errors which is theoretically sound and which is shown above to give results independent of the frequency and of grounding on all cells except those with very low cell constants, we have thought it unnecessary for our present purposes to analyze further the relative importance of each of these errors. We have decided, therefore, that for precision measurements of the conductivity of solutions, oil must be used instead of water in the thermostat and the drawbacks of oil must be tolerated or remedied as much as possible by a reconstruction of the stirring mechanism and regulators and heaters and by adding cooling coils to take the place of the cooling effect of evaporation in a water thermostat.

Conditions of Balance of the Bridge Analyzed

We will now substitute $Z = R + jX$ in the general condition of balance of the bridge, $Z_1/Z_2 = Z_3/Z_4$, giving

$$\frac{R_1 + jX_1}{R_2 + jX_2} = \frac{R_3 + jX_3}{R_4 + jX_4} \tag{3}$$

Clearing of fractions, remembering that $j^2 = -1$, and separating the horizontal and vertical components gives

$$R_1R_4 - X_1X_4 = R_2R_3 - X_2X_3, \text{ and} \tag{4}$$

$$R_1X_4 + R_4X_1 = R_2X_3 + R_3X_2 \tag{5}$$

which are conditions that must be satisfied to obtain a sharp balance of the bridge. It is generally assumed that at balance

$$R_1R_4 = R_2R_3 \tag{6}$$

but this in general is not true, and will only be true if the precautions which are shown below to be necessary are observed. It will be proved below that the apparatus commonly used is imperfect in this respect.

In the light of these equations there are three possible plans of bridge design and operation.

1. Construct the bridge so that both the resistance and reactance are known in three of the arms, that is, in the two ratio arms and in the arm containing the resistance box, and then both the resistance and reactance of the cell can be computed from the two equations of balance. Or, expressed mathematically, if R_1, R_3, R_4, X_1, X_3 and X_4 are known, R_2 and X_2 can be computed from the two conditions of balance [Equations (4) and (5)]. This is the method suggested by Taylor and Acree. Although this method is theoretically sound there are serious experimental difficulties in carrying it out. The reactance is a function of inductance, capacitance and frequency. If the resistance, inductance and capacitance are all in series, then $X = L\omega - 1/C\omega$, where X is the reactance in ohms, L the inductance in henrys, C the capacitance in farads, $\omega = 2\pi f$, and f is the number of cycles per second. If the capacitance is in parallel with the resistance, a more complicated relationship holds which will be explained below.

There may be both inductance and capacitance in each arm and it is difficult to measure these quantities with precision, especially in the presence of each other and of a high resistance. Moreover, the frequency would have to be measured or otherwise known accurately whenever the bridge is used, which would add undesirable complications to the experiments. Furthermore, if R_2 must be computed from Equations (4) and (5), the bridge cannot be made direct reading.

2. Equation (4) can be transformed into

$$R_2 = \frac{R_1R_4}{R_3}\left(1 - \frac{X_1X_4 - X_2X_3}{R_1R_4}\right) \tag{7}$$

where the expression inside the parentheses may be regarded as a correcting factor. It is obvious that this correcting factor should be avoided if possible but it should be avoided by designing the bridge so as to make the correction negligible, not merely by ignoring it as is the common practice.

It is evident from Equation (7) that if the bridge can be designed and built so that the reactances of any two adjacent arms (for instance, the two ratio arms 3 and 4) are negligible so that we can write $X_3 = X_4 = 0$, then the correcting factor becomes 1 and drops out. This means that the two ratio arms should be pure resistances free from inductance and capacitance; but it would be very difficult to carry out this ideal in practice, especially if it is desired to make the ratio arms variable in resistance.

However, it would be a mistake to assume from Equation (7) that if $X_3 = X_4 = 0$, then the reactance in arms 1 and 2 is a matter of indifference because Equation (5) must also be satisfied at balance. If we substitute $X_3 = X_4 = 0$ in Equation (5), we obtain $R_4X_1 = R_3X_2$. Then if we have an equal arm bridge $R_3 = R_4$ and therefore $X_1 = X_2$ is a condition of balance; but X_2 is the equivalent series reactance in the cell which is due to capacitance and which cannot be made equal to zero rigidly (although we have found means to reduce X_2 substantially below the usual previous practice as will be explained in the second paper of this series), therefore a variable condenser must be placed in arm 1 in order to bring $X_1 = X_2$.

3. Even if the ratio arms cannot be constructed so that they have no reactance, there is an advantage in making them as nearly as possible identical in resistance and reactance. Equations (4) and (5) can readily be transformed algebraically into the following forms

$$R_1R_4\left(1 - \frac{X_1X_4}{R_1R_4}\right) = R_2R_3\left(1 - \frac{X_2X_3}{R_2R_3}\right) \tag{8}$$

$$R_1R_4\left(\frac{X_1}{R_1} + \frac{X_4}{R_4}\right) = R_2R_3\left(\frac{X_2}{R_2} + \frac{X_3}{R_3}\right) \tag{9}$$

but a balance may be obtained without satisfying the relationship $R_1R_4 = R_2R_3$, as may be shown in the following manner. Even if $R_1R_4 \neq R_2R_3$, dividing (9) by (8) gives

$$\frac{\dfrac{X_1}{R_1} + \dfrac{X_4}{R_4}}{1 - \dfrac{X_1X_4}{R_1R_4}} = \frac{\dfrac{X_2}{R_2} + \dfrac{X_3}{R_3}}{1 - \dfrac{X_2X_3}{R_2R_3}} \tag{10}$$

which is a condition which must be met to secure a balance. But X_1/R_1 is the tangent of the angle of phase displacement in arm 1, or the tangent of the angle by which the voltage leads the current in arm 1, or

$$\tan \theta_1 = X_1/R_1 \tag{11}$$

Therefore the above condition of balance may be written

$$\frac{\tan \theta_1 + \tan \theta_4}{1 - \tan \theta_1 \cdot \tan \theta_4} = \frac{\tan \theta_2 + \tan \theta_3}{1 - \tan \theta_2 \cdot \tan \theta_3} \tag{12}$$

and hence by a general rule of trigonometry

$$\tan (4 + \theta_4) = \tan (\theta_2 + \theta_3) \tag{13}$$

or

$$\theta_1 + \theta_4 = \theta_2 + \theta_3 \tag{14}$$

is a condition which must be met to secure a balance. This condition may be realized experimentally even if R_1R_4 is not equal to R_2R_3.

From an inspection of equations (8) and (9) it will be evident that the relationship $R_1R_4 = R_2R_3$ (which is commonly but erroneously assumed to be true at balance in any bridge) cannot be true unless both of the following relationships hold:

$$\frac{X_1X_4}{R_1R_4} = \frac{X_2X_3}{R_2R_3} \text{ and } \frac{X_1}{R_1} + \frac{X_4}{R_4} = \frac{X_2}{R_2} + \frac{X_3}{R_3} \tag{15}$$

and it is easy to show by algebraic analysis that both of these relationships cannot be true unless either

$$\text{(a)} \quad \frac{X_1}{R_1} = \frac{X_2}{R_2} \text{ and } \frac{X_3}{R_3} = \frac{X_4}{R_4}, \text{ or} \tag{16}$$

$$\text{(b)} \quad \frac{X_1}{R_1} = \frac{X_3}{R_3} \text{ and } \frac{X_2}{R_2} = \frac{X_4}{R_4} \tag{17}$$

An equivalent way of stating the conditions that must be met to make the simple relationship $R_1R_4 = R_2R_3$ valid is

$$\text{(a)} \quad \theta_1 = \theta_2 \text{ and } \theta_3 = \theta_4, \text{ or} \tag{18}$$

$$\text{(b)} \quad \theta_1 = \theta_3 \text{ and } \theta_2 = \theta_4 \tag{19}$$

It will readily be seen that this is a special case of the general condition of balance deduced above. Therefore, the conclusion of this analysis may be stated as follows. The simple relationship $R_1R_4 = R_2R_3$ is valid only if the bridge has been so constructed and balanced that the phase angle between the voltage and the current is the same in two pairs of adjacent arms of the bridge. (If this condition is not met then the sum of the phase angles in the two pairs of opposite arms must be equal and Equations (4) and (5) must be used to compute R_2.) One-half of this requirement to make $R_1R_4 = R_2R_3$ can be met by making the two ratio arms as nearly as possible pure resistances and as nearly as possible identical in resistance and construction so that any unavoidable reactance will be the same (that is, $X_3/R_3 = X_4/R_4 =$ very nearly zero). The reactance in the cell (X_2) should be made as small as possible but in general cannot be reduced to zero, and therefore provision must be made to introduce a controllable reactance (X_1) into the arm containing the variable resistance R_1. Then at balance $X_1/R_1 = X_2/R_2$ and $R_1R_4 = R_2R_3$ and, since $R_3 = R_4$, therefore $R_1 = R_2$.[12]

A bridge built in this way can be made direct reading since the unknown resistance of the cell, R_2, will be the same as the reading of the box, R_1. This is a very great advantage in the practical use of the bridge as it avoids the calculations necessary with bridges using variable ratio arms.

The foregoing theoretical analysis was stimulated by some experiments on the slide wire which is made by Leeds and Northrup for use as the variable ratio arms of a bridge (No. 4258 of their catalog No. 48, 1924)

[12] It should be clear that R_1 and X_1 (R_2 and X_2) are that pure resistance and that pure reactance which when placed in series are electrically equivalent (that is, give the same impedance and phase angle) to the impure resistance and the impure capacitance actually used even if connected in parallel. (See page 1075.)

and which has been much used in precision work, although it has also been criticized by others.[13] This bridge has a wire wound in a helix with ten turns each 15 cm. in diameter and with extension coils at each end and a sliding contact attached to the cover which moves up and down with the slider. The helix is the geometrical form most favorable for creating inductance and there is a heavy mass of metal in the center of the helix in which weak eddy currents will be generated, thus dissipating electrical energy as heat outside the bridge circuit proper and influencing the effective alternating current resistance of the helix, This inductance, although equally divided between the ratio arms when the slider is at the mid-point, is unequally divided with any other setting and the asymmetry is a function of the setting of the slider. Moreover, in this instrument there is mutual inductance between the two ratio arms. It becomes of interest, therefore, to determine whether or not this unbalanced inductance is great enough to cause an error in the measurement of the resistance and whether or not it can be compensated by capacitance without introducing an error in the resistance balance.

In the older form of this instrument the drum is of marble and the cover is of metal electrically connected with the sliding contact, thus introducing some capacity as well as a path for induced currents. The end coils are wound in four sections apparently according to the specifications of Curtis and Grover.[14] In the newer and supposedly improved form of the instrument the drum and cover are of Bakelite and the extension coils are apparently bifilar wound in two layers on thin wooden spools (see the section below on resistances). As compared with the older form the capacitance in the coils is presumably greater and the capacitance in the cover less; but any attempt to compensate inductance by a capacitance in the instrument has the drawback that inductance and capacitance are different functions of the frequency.

In the experiments recorded below the newer type of slide wire with the extension coils in the circuits was used as the ratio arms. The wire had a resistance of 6.60 ohms and each extension coil 30.1 ohms. Arm 2 consisted throughout of 30,000 ohms in a good resistance box shunted by an air condenser set so that there was approximately 55$\mu\mu$f. capacitance in the condenser. Arm 1 consisted of a variable resistance box of the same type shunted by a similar calibrated condenser. In the successive experiments this box was adjusted so as to give readings at various points on the slide wire. The exact balance was next found using direct current and a galvanometer. Then without changing either resistance, alternating current of 2400 cycles was substituted, the galvanometer was

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[13] See especially Morgan and Lammert, THIS JOURNAL, 48, 1231 (1926), and other references given there.

[14] Curtis and Grover, *Bull. Bur. Standards,* 8,495 (1912).

replaced by a telephone and a new balance obtained by a slight movement of the slide wire and adjustment of the condenser in arm 1. The following table shows difference between the alternating current and direct current reading in per cent. and the approximate capacitance in arm 1 at balance. A. C. error is error in measuring R_2 (assuming R_1 to be known) by the use of A. C. (2400 cycles) as compared with direct current. R_2 is computed as usual by the simple formula $R_1R_4 = R_2R_3$.

TABLE II

TEST ON LEEDS AND NORTHRUP SLIDE WIRE WITH 2400 CYCLES

Slide wire reading with D. C.	Slide wire reading with A. C.	Capacitance in arm 1 in $\mu\mu$f.	A. C. error, %
0.387	0.367	104	−0.082
2.757	2.748	75	− .036
4.082	4.079	59	− .012
4.804	4.805	...	+ .005
4.930	4.930	49	.000
5.174	5.175	45	+ .004
5.753	5.757	40	+ .016
7.313	7.324	29	+ .044
9.477	9.500	24	+ .092

These experiments show that with alternating current there is a systematic variation in the capacitance required in arm 1 and also show that there is an error in the bridge setting which is a function of the position of the sliding contact; it amounts to 0.1% at the ends of the bridge and cannot be compensated by the condenser without an error in the resistance balance.

We have made many similar experiments with variations but it does not seem worth while to publish these data in detail because the final outcome was a decision to reject this type of instrument entirely in favor of a better form which we have devised. These results will, therefore, be given only in the form of curves in Figs. 4 and 5. Curve A is the plot of the data given above. Curve C shows the results with 1000$\mu\mu$f. in arm 2 instead of 55$\mu\mu$f. The results of using the metal cover from the older instrument with the helix and extension coils of the newer instrument, with 55$\mu\mu$f. in arm 2 are shown in Curve B and with 1000$\mu\mu$f. in Curve D. This is an improvement. Fig. 5 gives similar data with the older form of instrument, with low capacitance in arm 1 (Curve H) and high capacitance (Curve P); and with the Bakelite cover belonging to the newer instrument on the old base with low capacitance (Curve G) and high capacitance (Curve E).

That this effect was due to the helix and not due solely to differences in behavior of the resistances used in arms 1 and 2 was proved by a similar experiment with a long straight slide wire which gave no such systematic variation. In the experiments with the straight wire slight variations between the direct and alternating resistance were found which depended upon the kind of box used but were not greater than 0.005% with the particular boxes used in the experiments recorded above and did not show the same systematic variation with the setting. The greater errors with the helical slide wire evidently show that this form of ratio arm is defective.[15] Evidently in this instrument in which a helically wound slide wire is used as a part of the ratio arms the phase angles in two ratio arms are not equal and independent of the setting, and the necessary conditions to permit the computation of the resistance by the simple formula, $R_1R_4 = R_2R_3$, are not satisfied with this apparatus. Moreover, the errors introduced by this defect are a function of the frequency, and therefore any apparent changes of resistance with frequency found by the use of this bridge are of questionable validity.

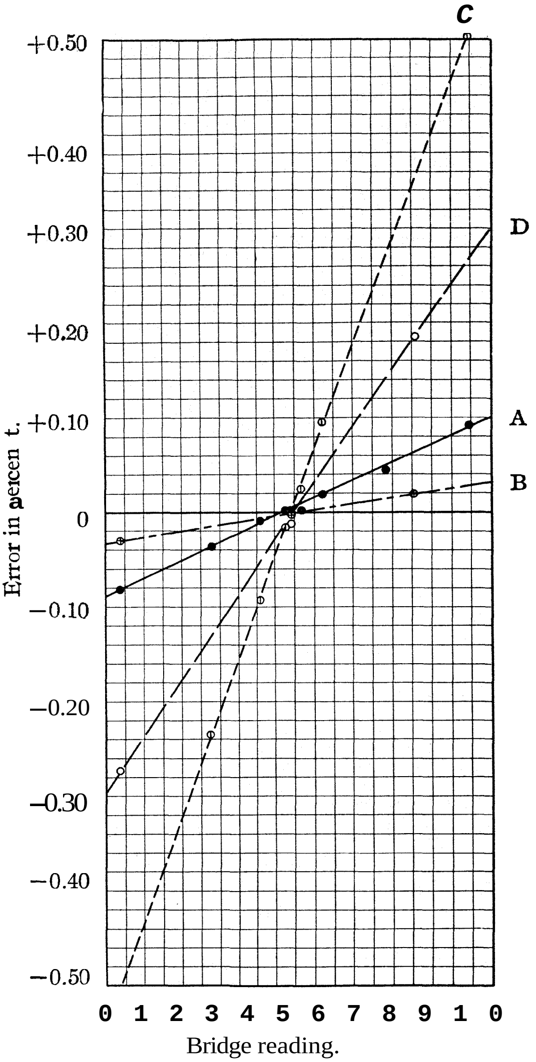

Fig. 4.—Errors caused by helical slide wire—Bakelite drum.

The presence of appreciable and variable reactance in the ratio arms obscures the interpretation of the reactance balance so that it has been ignored by most chemists.[1b,c] With our new form of bridge in which this disturbance of the reactance is eliminated the amount of capacitance required in arm 1 (C_1) becomes a measure of the reactance in the cell which is a function of cell design, method and extent of platinization

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[15] Of course this criticism does not apply at all to the use of a helix of similar construction in the Type K Potentiometer which is intended for use with direct current.

and the frequency. As will be explained in detail in the second paper in this series, the reactance balance has given us a measure of the quality of the platinization and has enabled us to devise a procedure for platinizing which gives an improvement in the results.

The Reactance Balance

In general there is some unavoidable capacity in the cell causing reactance (X_2), and, therefore, even with identical ratio arms some reactance must be introduced into arm 1 (X_1) so that $X_1/R_1 = X_2/R_2$ in order to obtain a sharp balance. This can be accomplished theoretically in three different ways.

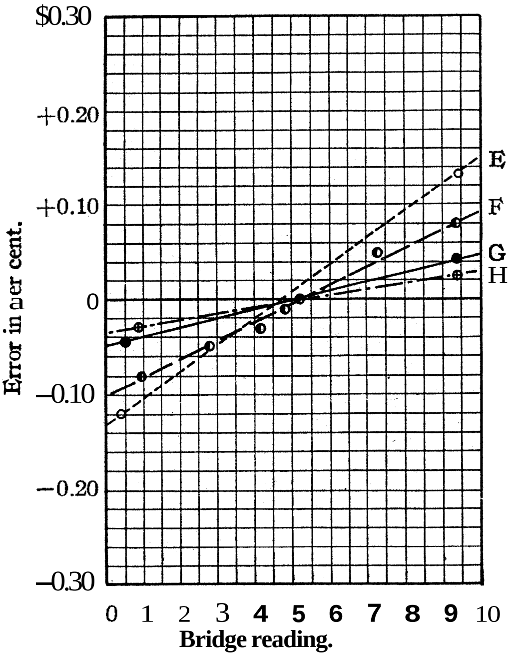

Fig. 5. —Errors caused by helical slide wire—marble drum.

1. Introduce inductance into the same arm of the bridge as the cell to compensate for the capacitance and thus make the reactance zero, as was done by Taylor and Acree. This method has the drawbacks that (a) it is difficult to construct a variable inductance whose resistance does not change appreciably with the frequency and the setting (so far as we know no such instruments are on the market); (b) a correction must be applied for the resistance of the variable inductance, and it is difficult to determine this A. C. resistance accurately in the presence of the inductance; (c) such variable inductances have a variable magnetic field which may influence the rest of the bridge and introduce errors.

2. **Put** a variable capacitance in series with the resistance box. This method is in practice not useful because the capacity required is enormous.

3. Put a variable capacitance in **parallel** with the resistance box. This is the method which was suggested by Kohlrausch and is generally used. In our judgment it is better than either of the alternative methods; but the theory of condensers indicates that there may be sources of error in this arrangement, and therefore it is important to determine whether with the available condensers at the working frequencies and resistances

the errors introduced thereby are great enough to require a correction to the box reading.

When a condenser is connected in parallel with a resistor, the resistance of the combination for alternating current is less than the direct current resistance or, in other words, even a perfect condenser has a shunting effect which diminishes the effective resistance. Furthermore, the condenser may not be perfect but may dissipate a significant amount of energy as heat in the dielectric. There may also be leakage along the surface of the insulator, which acts as an additional shunt. This will commonly be negligible except in very humid weather.

Such a real condenser may be considered as an ideal perfect condenser with a high resistance, R_P, in parallel. In a well-designed air condenser this parallel resistance depends primarily on the design and materials of the insulators used and not on the setting of the plates, and is therefore essentially a constant for any given instrument, independent of the setting; but the parallel resistance is inversely proportional to the frequency.

We may consider the arm 1 as being composed of three branches in parallel: the resistance box, R_R, an ideal perfect variable condenser, C_1, and a constant high resistance, R_P. The parallel resistance of the condenser, R_P, can be measured easily with a capacity bridge. In a good low loss condenser such as may be purchased it should be at least 10^9 ohms at 1000 cycles. The influence of the condenser resistance may be computed by the formula

$$R = R_R\left(1 - \frac{R_R}{R_P} + \ldots\right) \tag{20}$$

Therefore, if R_P is 10^9 it may be neglected without producing an error greater than 0.001% if R_R is not greater than 10,000 ohms. In the condenser which we used R_P was found by measurement to be 3×10^9 ohms and therefore the effect of its parallel resistance was negligible in all measurements up to 30,000 ohms at 1000 cycles and up to 10,000 ohms at 3000 cycles.

It now remains to consider the shunting effect of a perfect condenser whose capacitance is C and reactance $X_c = 1/\omega C$. According to the law of parallel branches

$$\frac{1}{Z} = \frac{1}{R_R} + \frac{1}{jX_c} \tag{21}$$

This may be transformed algebraically into

$$Z = R_R\left(\frac{X_c^2}{R_R^2 + X_c^2}\right) + jX_c\left(\frac{R_R^2}{R_R^2 + X_c^2}\right) \tag{22}$$

where the first term is the equivalent series resistance of the combination and the second term gives the equivalent series reactance of the combination. Therefore, unless R_R^2 is negligible in comparison with X_c^2, a correction must be applied to the reading of the resistance box, R_R, on account of the shunting effect of the parallel condenser. But we may write $X_c^2 = 1/C^2\omega^2$ and therefore the correcting factor becomes $1/(1 + R_R^2C^2\omega^2)$. Therefore with sufficient accuracy

$$R = R_R(1 - R_R^2C^2\omega^2 + \ldots.) \tag{23}$$

We have found that with our improved bridge the neglect of this correcting factor will not make an error of as much as 0.001% except under extreme conditions, but it may become appreciable at high resistances, high frequencies or with unplatinized electrodes which require a high parallel capacitance in another arm to balance their reactance. Thus if the condenser reading is 100$\mu\mu$f. and the resistance 30,000 ohms and the frequency 2500 cycles, this factor becomes 1/1.0022, so that an error of 0.22% would be made by ignoring this correction. But if 50 $\mu\mu$f. were required while measuring 10,000 ohms with 1000 cycles, the factor would be 1/1.00001, or an error of only 0.001%. The following table shows the capacitance which may be present as a shunt across the resistance box without causing an error of more than 0.001% from this cause at the resistances and frequencies indicated.

TABLE III

CAPACITANCES IN SHUNT WHICH REQUIRE A CORRECTION OF 0.001%

Resistance	Capacitance in micromicrofarads at 1000 cycles	at 2500 cycles
100	5000	2000
500	1000	400
1000	500	200
5000	100	40
10,000	50	20
30,000	17	7

Very few of the previous workers on conductivity record the capacitance required to adjust their bridges to balance and therefore it is impossible to determine whether or not this error was significant, but it is a function of the resistance, of the frequency and of the capacitance, and the latter is a function of the cell design and of the grounding of the thermostat. Therefore, any conclusions drawn by earlier workers as to an apparent change of cell constant with frequency or with change of concentration of the solution contained therein cannot be accepted without reserve pending further examination with the improved bridge and with an allowance if necessary for this source of error. Such an experimental study is now in progress in this Laboratory.

The cell itself contains a reactance and therefore it might be argued that the effective resistance of the cell is changed in the same way as the resistance shunted by a condenser in arm 1, so that these effects would compensate each other and make a correction unnecessary. Whether this is true or not depends on the mechanism which produces the reactance in the cell. If the capacitance of the cell is due to a gas film on the electrodes then this is in series and requires no correction. Reversible polarization is also probably equivalent in electrical effect to a series capacitance although it may not be the same function of the frequency as a condenser and it may not be harmonic. True geometrical capacitance between large electrodes close together is presumably in parallel with the resistance. This matter will be discussed more in detail in the second paper of this series. It is generally considered that in a cell the capacitance and resistance are in series and the fact that variations in frequency require variations in capacitance in arm 1 to secure a balance indicates that the mechanism of the capacitance in the cell is different in the cell than in arm 1. Whatever decision is finally made about the capacitance in the cell, it seems best to apply the correction in arm 1 if it is significant.

Resistance Boxes

Much to our astonishment and dismay none of the resistance boxes which were available to us proved to be entirely suitable for work of the precision for which we were aiming. The study of the cause of the defects and the design and construction of an improved box caused a considerable and unexpected delay in our program. The resistance box is probably the most important part of the bridge because it is the working standard on which all of the measurements depend.

In our preliminary experiments, after every part of the earlier bridge except the resistance boxes had been investigated and perfected, it was found that the A. C. balance was different from the D. C. balance. This difference was found in all cases in which two boxes of different make or type were compared with 10,000 ohms or more in use and in a few cases with resistances as low as 1000 ohms. We did not detect the effect with the 100 ohm coils except in one box of poor quality. By interchanging the two resistance boxes it was proved conclusively that the trouble was in the boxes rather than in the bridge. Since the balance with direct current doubtless gave the true relative resistances, the deviation when using alternating current must have been due to some error which we call the alternating current error. For example, in one series of experiments we compared a box made by Leeds and Northrup containing Curtis coils, Type 4238 (hereafter called Box C), with a five dial box made by the General Radio Company, Type 102 (Bulletin 2050), which was supposed to be suitable for this work (called by us Box D). At this stage of our work we assumed that the Curtis coil box was free from A. C. errors. (This assumption was later proved to be very nearly although not rigidly true. See Table IV.) The resistance of the 10,000-ohm coil in box D was 2.5 ohms less when measured with 2400 cycles than when measured with direct current, or its A. C. error was −25 parts per 100,000. In this box there was a wire leading from one binding post to the other end of the box which passed very close to the coils and other wiring. After this wire had been removed and replaced by another at as great a distance from the other wires and coils as the space inside the box permitted, but without changing anything else, the error was −1.1 ohms. After removing the varnished cotton insulation from the wiring inside the box the error was −0.5 ohms. The leads from the 10,000-ohm coil to the contact studs in the box were entirely disconnected and the leads connected directly to the bridge. The error was then +0.2 ohms (+2 parts per 100,000) compared with the 10,000-ohm Curtis coil as mounted in its box. This reversal of the sign was of great interest as it suggested that the Curtis box which we had been using as a standard of reference may have an error. Then the 10,000-ohm G. R. coil was removed and mounted by itself on a hard rubber panel in the same manner as in the box. This coil and the Curtis coil in its box were now identical. Since the mounting could not have improved the coil this indicates that the Curtis box must have a small negative error. Furthermore, this G. R. coil had been previously measured in its box in a mounting similar in all respects except that other coils were appended thereto and then gave an error of −0.5 ohms. This indicated that appended coils which were connected at one end to the coil measured but which were not in the circuit proper were nevertheless capable of causing an alternating current error.

In order to determine the magnitude of these errors and to locate them definitely and in order to determine their cause, it was necessary to have some standard of reference so designed as to be as free as possible from these errors.

The most nearly pure resistance is a short, straight, thin wire of high specific resistance. We realized this in the form of a thread of mercury in an extremely fine capillary tube of Pyrex glass. A piece of small bore, thick walled Pyrex tubing about 2.5 cm. long was sealed at each end to a tube of some 5 mm. internal diameter, the central portion was heated until it was about to collapse and then quickly drawn out to about 40 cm., thus giving a very fine capillary tube. The end tubes were then bent at right angles to the capillary for convenience in filling. Mercury was then put in one end tube and attached to a source of compressed air at a pressure of 90 pounds per square inch. About half of the tubes proved to be completely closed, whereas others had too coarse a capillary to be useful. The best of many required several hours before the mercury appeared at the other end of the tube and when measured was found to have a little more than seven thousand ohms' resistance. Several others having smaller resistance were also made. These tubes were then mounted on a suitable frame for mechanical support and immersed in oil in order to control the temperature without introducing the undesirable secondary effects which would have been caused by mounting in water. These mercury threads have a high temperature coefficient, a low heat capacity, and poor heat conductivity through the relatively thick glass walls; they do not remain constant over long periods and cannot be adjusted to convenient round values of resistance; but in spite of these drawbacks there is a strong theoretical presumption that they have the same resistance with direct current as with alternating current up to at least 3000 cycles and, therefore, they have proved to be very useful in testing the behavior of resistance boxes with alternating current.

Then with the aid of these mercury threads and of our new bridge, which was built after the preliminary experiments described above, we were able to determine the difference between the A. C. and D. C. resistances of the various boxes available to us. Some of the results are shown in Table IV.

Box A. A Leeds and Northrup plug-box type, which is not designed for use with alternating current and is not even listed in their Catalog No. 48, "Apparatus for Measuring Conductivity of Electrolytes." These boxes have been used for the purpose and it was therefore of interest to determine the error in this type when used with alternating current.

Box B. A new type of box made by Leeds and Northrup. Type No. 4784, for use with alternating current. It is a six decade dial box with all switches enclosed inside the box. It is well designed mechanically.

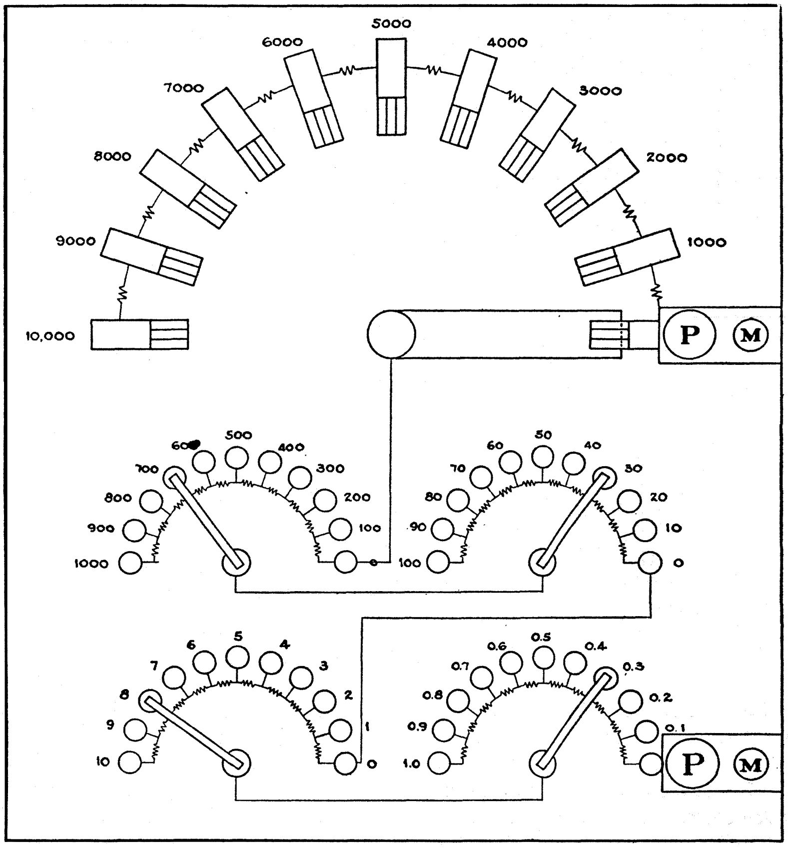

Fig. 6.—Resistance Box E.

Box C. A resistance box built by Leeds and Northrup, Type No. 4238, containing Curtis coils of manganin and recommended by them for use in measuring the conductivity of electrolytes. It is not a dial box and the leads from each coil are brought to separate binding posts so that any coil not in use is disconnected from all others. It covers the range 1000–40,000 ohms in steps of 1000 ohms. It is an inconvenient box to use, especially in a direct reading bridge. It is the box which served as our provisional standard referred to above.

Box D. A box built by the General Radio Company, which has been used in the preliminary experiments and improved by modification. In addition to removing the varnished cotton insulation and rearranging the internal wiring as described above, half of the 10,000-ohm coils had been removed and the remainder attached to the terminals in such a way that the 10,000-ohm coils which were not in use were not appended to the coils which were being used. It had in addition four lower decades with dial switches connected as usual, so that the coils not selected for use by the switches are appended. The 100-ohm and 1000-ohm coils were wound by the method suggested in principle by Ayrton and Mather[16] and perfected by the General Radio Co. To make a 1000-ohm coil by this method an insulated manganin wire having 2000 ohms resistance is wound on a thin Bakelite card with spaces left between turns equal to the diameter of the wire.

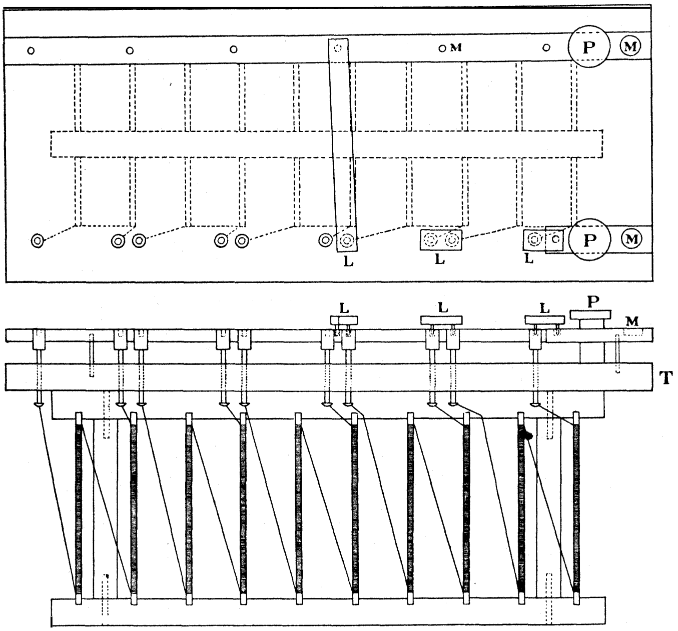

Fig. 7.—Resistance Box F.

Then another similar wire is wound on the same card starting at the same end as the first wire but rotated in the opposite direction so that on the edge of the card the second wire fills the spaces left between the turns of the first wire. These two wires of course cross each other twice in every turn. These two wires are then connected at the ends so that they are electrically in parallel. The inductance of the coil is low because the two portions oppose each other inductively and because the area enclosed by the coil is small. The distributed capacity is low because the adjacent turns are at nearly the same potential during use. The 10,000 units were each made up of two 5000 ohm coils in series, wound inductively on thin Bakelite cards. All these coils were made of manganin.

Boxes E and F. Two new boxes built in our shop which are described in detail below and shown in Figs. 6 and 7. The coils were similar to those in box D, the only difference in the boxes being in the mounting and switches.

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[16] Ayrton and Mather, Proc. *Phys. Soc.*, 11, 269 (1892).

TABLE IV

ALTERNATING CURRENT ERRORS IN CERTAIN RESISTANCE BOXES

A. C. RESISTANCE—D. C. RESISTANCE IN PER CENT.

Box	Resistance measured	Error at 1100 cycles	Error at 2400 cycles
A (L & N plug type)	5000	−0.012%	−0.032%
B (L & N dial new type)	5000	− .002	− .003
	9000	− .005	− .007
	10,000	− .006	− .011
	20,000	− .009	− .016
	30,000	− .013	− .019
Unmounted 10,000-ohm coil of this type		− .004	− .008
C (L & N Curtis box type 4238)	10,000	− .002	− .003
	20,000	− .003	− .004
	30,000	− .005	− .007
D (G. R. dial modified)	ten 1000 coils	− .002	− .004
	10,000	− .002	− .003
	20,000	− .006	− .008
E (Our new box) Fig. 6	ten 1000 coils	.000	.000
F (Our new box) Fig. 7	10,000	.000	.000
	20,000	.000	− .001
	30,000	− .002	− .003

These experiments showed that none of the makes of resistance box which were available to us is free from alternating current error. The best of the boxes available by purchase which was tested was the box containing Curtis coils, C, and the second best was the modified General Radio box, D. In all of the boxes the percentage error increases with the resistance. In all of these boxes (except A which was not designed for A. C.) this effect is negligible at 1000 ohms and below. The fact that these errors finally turned out to be all negative and to increase with frequency is extremely significant because it shows that the cause is dielectric loss in the insulator. Skin effects and eddy currents would make the alternating current resistance greater than the direct current resistance. A capacitance if pure would cause no error in the resistance except for the shunting effect which is probably negligible in this case (see Equation 23 and Table III); but an alternating electric field across any dielectric except air is always accompanied by an irreversible dissipation of energy as heat within the dielectric medium, commonly called the dielectric loss, which has the effect of an increase of conductance or a decrease in resistance. The error due to this dielectric loss is approximately proportional to the resistance across which it is shunted, the capacitance, the frequency and the power factor of the particular kind of substance within the electric field; or, expressed mathematically

$$R = R_R\,(1 - R_R\,C\omega\eta + \ldots) \qquad (24)$$

The resistance and frequency are not controllable factors in the design of boxes, but it should be noted that greater care must be taken with the high resistance coils.

Air has a power factor essentially zero and therefore the box should be constructed so as to bring the strong dielectric fields in air as much as possible. Some solid dielectric is, however, essential for mechanical support but care should be taken to use no more than is required to produce sufficient mechanical rigidity, to have the supports where the electric fields are weak, if possible, and to use only the better dielectrics. Conductance along the surface of the solid dielectric in condensers or resistance boxes may also cause an error but is not likely to be troublesome except on occasions when the weather is abnormally humid. Bakelite is superior to hard rubber in this respect. Coating the surface with a thin layer of paraffin helps to avoid error from this cause.

We are indebted to Professor R. F. Field of the Cruft Laboratory for making available to us the results of an investigation, as yet unpublished, on the power factors and dielectric constants of many insulators at both audio and radio frequencies. Professor Field has kindly consented to the publication of selections from his data which are especially pertinent in designing resistance boxes and condensers. These values vary only slightly with the frequency within the audio range.

TABLE V

POWER FACTORS AND DIELECTRIC CONSTANTS OF INSULATORS AT 1000 CYCLES FROM HITHERTO UNPUBLISHED MEASUREMENTS BY PROFESSOR FIELD

Material	Power factor	Dielectric constant
Sulfur	0.0001	2.7
Paraffin	.0001	2.3
Mica	.0008–0.0015	5.9–6.8
Hard rubber	.004	3.5
Pyrex glass	.0055	6.3
Transparent Bakelite	.0063	5.6
Transparent Bakelite, another specimen	.0073	5.2
Transparent Bakelite, another specimen	.026	6.2
Common sheet Bakelite	.1	8
Silk cloth	.06	2.2
Cotton cloth	.16	2.1

Hard rubber and selected specimens of transparent Bakelite are the best available materials with suitable mechanical properties for panels to support coils, terminals, switch contacts and switches.

The factor of the error due to dielectric loss which can be most readily reduced in the design is the capacitance. The capacitance is proportional to the dielectric constant of the insulator and therefore a material with low dielectric constant should be used. Hard rubber is the best of the available materials in this respect. By spreading apart the switch contacts and all connections which pass through the solid dielectric the capacitance can be reduced. The capacity between two points is inversely proportional to the square of the distance and between plates inversely proportional to the distance apart. In designing our boxes we have used a purely empirical rule that the distance between contacts, binding posts or the shafts of switches should be at least 0.04 $\sqrt{R}$ cm., where R is the resistance mounted between these same contacts. This rule applies where the areas of the conductors are small (as for example a No. 4 screw) and where there are not many of these capacitances.

The quality of the coils to be used must be considered, as well as the mounting. A capacitance inside the coil, even if compensated by inductance, may cause a dielectric loss. For the 10-ohm or lower decades any moderately good coil, such as the common bifilar winding on a wooden spool, is good enough. But the common bifilar winding is not satisfactory in the 100-ohm and 1000-ohm decades because dielectric losses become significant and because the capacitance in the box may exceed the capacitance in the cell, necessitating a condenser across the cell, which is undesirable. Fortunately, there are available by purchase two kinds of coils which are entirely satisfactory in the 100-, 1000- and 5000-ohm units. Both the Curtis coils such as are used in the Leeds and Northrup box (Type 4238 or 4656) and the coils made by the General Radio Company were found to have essentially the same resistance with direct current as with alternating current up to 2400 cycles when tested with our mercury thread resistances. The General Radio 100-ohm and 1000-ohm coils are wound according to the Ayrton principle. The 5000-ohm coils are wound inductively on flat cards of Bakelite. Two of these in series make each 10,000-ohm unit. The Curtis coils which we tested were adjusted more closely to their nominal values than others but this is a matter of convenience rather than precision; the greater care in adjustment and the more complicated method of winding make the Curtis coils much more expensive. In all of these coils the wires are so thin that skin effects are negligible at the frequencies of interest to us.

Akin to the error caused by dielectric loss in the insulation is the error caused by appended coils. In the usual form of switch or plug box the coils which are not in use, although not in the circuit, are nevertheless attached at one end to the coils which are in use. This arrangement is unobjectionable with direct current but with alternating current it permits current to flow into the appended coils sufficient to charge the capacitance between the appended coils and the rest of the circuit, and this current reverses itself twice in every cycle. This charging current passes through the resistance of the coils themselves and therefore dissipates energy as heat and thus influences the apparent resistance. It is in effect an additional branch consisting of a small capacitance and a high resistance in parallel with the coils in use and therefore acting like a shunt diminishes the effective resistance of the combination. In Table VI are shown the results of some experiments demonstrating the existence of this source of error. Coils totaling 30,000 ohms in the General Radio box D were measured with A. C. and with D. C. with various coils appended.

TABLE VI

ALTERNATING CURRENT ERRORS DUE TO COILS APPENDED TO 30,000 OHMS, IN PER CENT.

Appended coils	Error at 1100 cycles	Error at 2400 cycles
Ten 1000-ohm Ayrtons	−0.002	−0.003
Ten 1000-ohm Ayrtons plus one 10,000 G. R.	− .003	− .006
Ten 1000-ohm Ayrtons plus two 10,000 G. R.	− .004	− .008

We were unable to detect the effect in a box containing a decade of 1000-ohm coils and three smaller decades. As the result of these experiments (only reported in part above) we decided that the coils in the 10,000-ohm decade should be completely disconnected at both ends when not in use, but that in the lower decade it was permissible to have the coils appended when not in use provided they were not mounted too close together. The possibility of errors due to dielectric loss and to appended coils is mentioned briefly by Curtis and Grover.

As a result of these experiments and theoretical analysis we concluded that the box for use in arm 1 of the bridge should meet the following specifications if possible.

1. The resistance of each coil and of any combination as mounted in the box and selected by the switches should be the same (within 0.001%) with direct current as with alternating current of any frequency up to the maximum to be used (say 3000 cycles per second) and the reactance should be as low as possible. In order to meet this specification the following conditions are necessary or desirable.

(a) The mutual capacitance between parts of the box should be low. This can be accomplished by using coils of suitable quality, mounted so as to avoid undue proximity of coils, lead wires and switch terminals, and by using insulators of low dielectric constant.

(b) Dielectric losses associated with the capacitance should be made negligible by designing the box so that strong electric fields do not occur in a dielectric other than air, by using the minimum amounts of solid dielectrics, and by using only dielectrics of low power factor.

(c) The inductance should be low, which is easily attainable by using good coils.

(d) Hysteresis and eddy current losses associated with the inductance should be made negligible by avoiding entirely the use of iron and by avoiding the presence of masses of metals of any kind within the magnetic field.

(e) The wire used in coils and lead wires must be fine enough so that skin effects are negligible; this presents no difficulty.

(f) Coils of 10,000 ohms or more must be entirely disconnected from the circuit when not in use.

Losses associated with the inductance are more easily avoidable than the dielectric losses associated with the capacitance. Therefore, in designing coils and boxes, special emphasis should be placed on keeping capacitance low and dielectric losses negligible. It should also be emphasized that the mere compensation of capacitance by inductance so that the coil has a small net reactance does not solve the problem, because such a coil or box may have an appreciable dielectric loss and therefore its effective resistance with alternating current will be different from its true direct current resistance and will be a function of the frequency.

2. The temperature coefficient of the box should be low, constant and known. Manganin and Advance wire are satisfactory in this respect.

3. For convenience the box should be of the decade type with dial switches in order that the bridge may be made direct reading by the use of equal ratio arms. In order to have the desirable range and precision it should have six decades, reading in tenths, units, tens, hundreds, thousands and ten thousands of ohms. To determine the hundredths and thousandths of an ohm we have devised a special sliding contact in the bridge which will be described below. We have found it desirable to mount the highest decade (tens of thousands of ohms) in a separate box with connections made by links dipping into mercury cups instead of dial switches in this box and have not yet found it necessary to have more than 50,000 ohms in this box, giving a total of 61,111 ohms in the two boxes. Each decade should have ten coils instead of nine as usual in order that the sum of all ten may be compared with the next higher coil during calibration.

4. The contact resistance in the switches and the resistance of the lead wires should be made as small as possible and should not vary more than 0.001 ohm during use.

5. The coils should be accurately adjusted to their nominal values. This is of relatively minor importance, however, as it is purely a matter of convenience, because any box will have calibration corrections which must be applied in precision work and it makes comparatively little difference whether these corrections are large or small. Insistence on close adjustment adds greatly to the cost of the box.

6. The coils should be so constructed, aged and protected against moisture and the fumes of a chemical laboratory that their resistance remains constant over long periods.

7. The thermo-electromotive force should be small. This is of no importance when using alternating currents but it is necessary to cali-

brate the box with direct current because the standard coils for which a Bureau of Standards certificate can be obtained are not designed for use with alternating current. Moreover, it is desirable to be able to compare alternating and direct current readings (with a metallic resistance in place of the cell as a means of proving the absence of error in the bridge). This is an argument in favor of using manganin; but if thermoelectric forces are unavoidable, error from this source can be avoided by the use of a reversing switch.

8. The switch terminals and lead wires connecting the coils and terminals must be so designed that the lead wires are included in the value of each coil in exactly the same manner for all settings of the switch and also permit each coil to be calibrated independently with the resistance of the lead wires included in exactly the same manner as in the actual use of the box.

We built two new boxes designed in accordance with these principles. One covering the range 0.1 to 11,111 ohms in steps of 0.1 ohms is shown in Fig. 6 which is a top view with the wiring shown diagrammatically. The top was made of hard rubber. The coils were made by the General Radio Company, wound on the Ayrton principle, of manganin wire. Standard General Radio dial switches were used for the 0.1-ohm, 1-ohm, 10-ohm and 100-ohm decades. The controlling factor which determines the radius of the switch for the 1000-ohm decade is the capacitance between the shaft of the switch and the contacts. This radius was 9 cm., which required a special switch. Ten coils were used in each decade instead of the usual nine. Care was taken in the arrangement of coils and lead wires inside the box to avoid dangerous proximity of wires differing greatly in potential. The terminals are provided with mercury cups, M, and binding posts, P.

The 10,000-ohm units were placed in an entirely different box (Fig. 7). The panel, T, and supports for the coils were of transparent Bakelite, which was selected because it is less hydroscopic than rubber. The panel was supported by a tight wooden box (not shown in the figure) enclosing the coils. Each 10,000-ohm unit consisted of two 5000-ohm coils wound inductively on cards of Bakelite. They were made of manganin wire by the General Radio Company. The lead wires from each end of each 10,000-ohm unit were 4 cm. apart where they passed through the panel and terminated in mercury cups. It was necessary to design the box so that any coil not in use was entirely disconnected from the circuit to avoid the effect of appended coils. Since a switch which would meet these specifications would be cumbersome and complicated we adopted a simple system of links, L, dipping into mercury cups, M, for this box. The coils in use were connected by short links and the last coil in use was connected by a long link to a bus bar across the box. With the links in the position shown in the diagram the resistance between the binding posts, P, would be 20,000 ohms. Only five 10,000-ohm units were assembled in this box as this seemed to be ample for any requirements that we wuld foresee. The terminals were provided with both binding posts and mercury cups for convenience and nickel plated to avoid spreading amalgam over the surface. The box when assembled and tested was found to be superior to any on the market, as is shown by the data in Table IV.

Description of the New Bridge

We have built a new bridge which is designed in conformity with the principles explained above and is also convenient and rapid in operation.

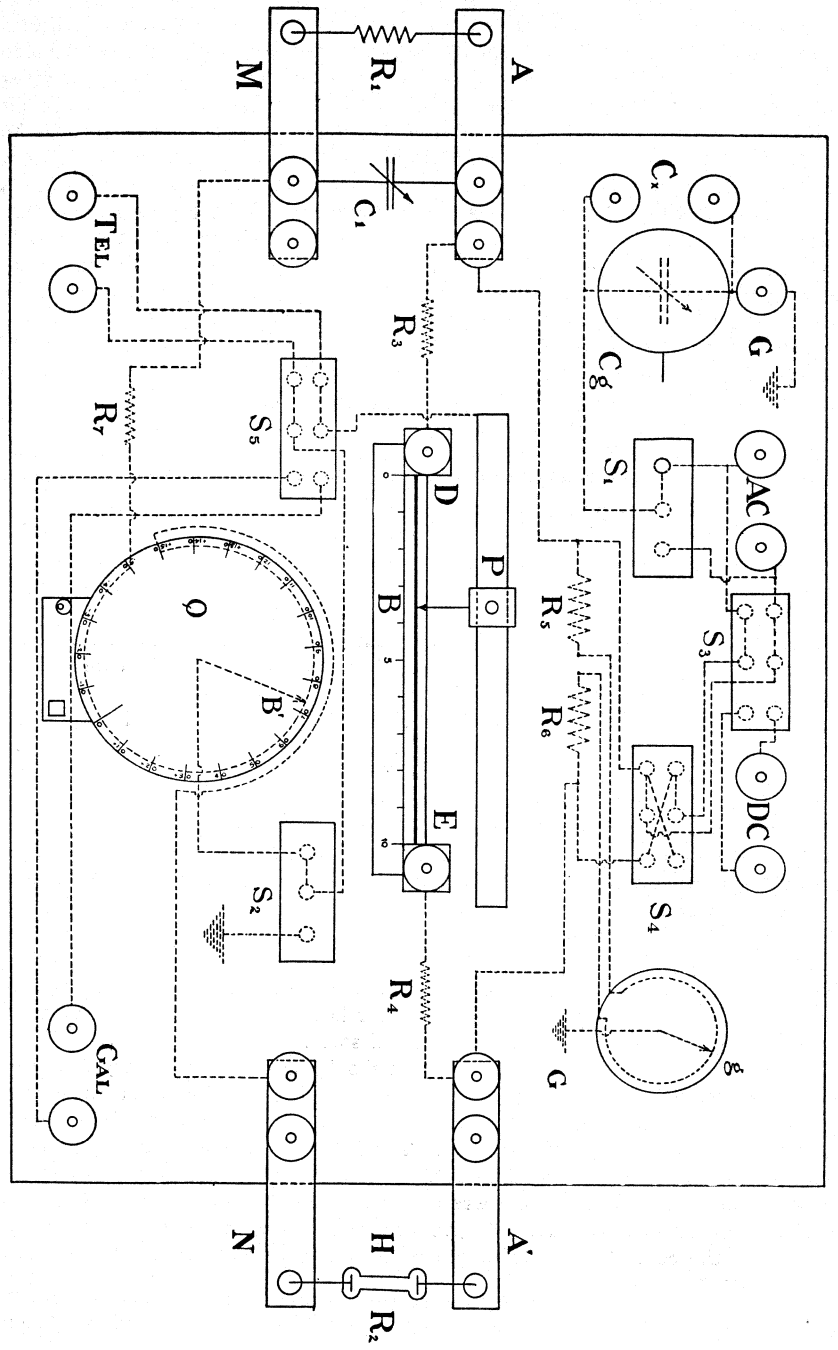
M
A
R1
C1
TEL
R3
S5
R7
Cx
G
Cg
S1
AC
S3
DC
S4
D
P
B
E
Q
B'
R5
R6
R4
S2
GAL
G
g
N
A'
H
R2

Fig. 8.—Bridge.

The bridge consists of a flat wooden box five inches deep and 13 X 17 inches in length and breadth, with a hard rubber top which supports all of the electrical parts. The coils, switch contacts, sliding contacts (with one exception) and ground condenser, Cg, are inside the box, protected from fumes and mechanical injury. The resistance box. R_1, is a separate unit and is connected to the bridge by heavy links dipping in mercury cups and the variable condenser, C_1, is also a separate unit and is shunted across the box. The oscillator, amplifier and telephone (or battery and galvanometer) are separate units which are connected at suitable binding posts. Everything else is built into the bridge. Fig. 8 gives the actual layout of the top of the box, showing the actual position of all binding posts, dials, scales and switches, with the wiring, where it is under the top. shown in dotted lines. Along the northern edge[17] are located the binding posts for the ground connection and for the A. C. and D. C. power lines, and a switch, S_3, to select one or the other; near at hand is the reversing switch, S_4. The double throw, double pole switches used were made by the Federal Telegraph and Telephone Company of Buffalo, N. Y., and are their Type No. 1425W. The grounding device, which is one of the novel features of the new bridge, is also placed in the northern part of the box. A variable air condenser, C_g, of $500\mu\mu f$. capacitance is mounted in the northwest corner, with dial and scale on top and plates inside. One side of the condenser is permanently connected to the post, which in turn is grounded. The other side of the condenser may be connected to either of the two alternating current power lines as may be desired by means of the switch, S_1. For ordinary use with our oscillator the capacity provided is large enough but in some abnormal cases, or when using other oscillators, we have found more capacity to be needed and we have, therefore, added two more binding posts, C_x, which make it possible to attach a larger condenser if needed. From the reversing switch, S_4, the current passes to the resistance part of the grounding device which is shunted across the line as shown. R_5 and R_6 are each a 1000-ohm coil of the Ayrton winding made by the General Radio Company. Between R_5 and R_6 electrically (and a part thereof in electric function) but placed in the northeast corner for convenience, is a manganin wire of about 0.75-ohm resistance wound in a single turn around a hard rubber cylinder with a sliding contact, g, which is always connected to ground. This slider is mounted inside the box but is controlled by a dial on the top. With this arrangement the possible variation in the ratio of R_5 to R_6 is 0.15%. This ratio must be approximately unity because $R_3 = R_4$, but the ratio is also influenced by losses and leakage to ground in the lead wires from the oscillator. For most cases, including all normal uses of the bridge, this possible variation of 0.15% is ample; but in a few unusual and abnormal cases the available variation was insufficient. It would therefore be better to make the resistance in this slide wire somewhat larger. This comparatively minor defect in our final bridge is the greatest which we have yet discovered in it. The remedy is easy if we ever have occasion to use the bridge under such conditions that this fault becomes troublesome.

The adjustment of the ground balance should be made with every measurement, otherwise erroneous results may easily be obtained, especially when measuring high resistances. This is well illustrated by some experiments which will be described in more detail in the second paper of this series. These experiments were planned to determine whether or not the resistance of a solution is a function of the voltage applied or of the current density. The resistance was measured with the new bridge and then an adjustment made in the oscillator to give a higher voltage and therefore greater current density in the cell. There was an apparent change of resistance of a few thousandths

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[17] The points of the compass are used for clearness and convenience in referring to the diagram, which may be regarded as a map. The actual orientation of the bridge is of no consequence.

of one per cent. but it was then found that the ground balance had changed greatly. On adjusting the ground balance correctly the bridge setting returned to its former value. Therefore without our improved method of grounding the bridge, we should have been in danger of drawing erroneous conclusions on this point. The inside of the northern third of the box was lined with sheet copper and grounded to serve as a shield for the electrical parts heretofore described. The bridge proper was not shielded.

From the ends of the shunt, R_5 and R_6, the power lines pass through a hole in the shield to the ends of the bridge proper, **A** and **A'**, which consist of heavy nickel-plated brass bars, mounted on top of the box and provided with a mercury cup and two binding posts each.

Between A and **A'** are mounted the ratio arms, AB and BA', consisting of two coils, R_3 and R_4, each a General Radio Ayrton coil of 1000 ohms mounted under the cover. These coils cannot be adjusted to exact equality and, moreover, they will change slightly with age. In order that the ratio arms may be adjusted to exact equality 15 cm. of a heavy (2 ohms per meter) manganin wire, **DBE,** with a sliding contact, B, is mounted between them. With this arrangement a movement of the slider of 1 mm. changes the ratio of the arms by four parts in a million. This wire is soldered to a heavy brass plate which is fastened to binding posts. Several interchangeable wires of different diameters and resistance are provided which increase the range of adjustment with this slider and adapt the bridge for special uses as a percentage differential bridge. A scale, also interchangeable, is indicated just south of the wire. This scale may be calibrated to read in percentage change in resistance or, if desired, as a differential thermometer. A sliding contact, B, makes connection with the heavy bus bar, P, and has a screw clamp which holds it in place after adjustment. The method of adjustment to make B the exact electrical center of the bridge will be described later. The resistance in the sliding contact is not in the bridge circuit proper, but only in the line to the detector.

To the south of **A** and **A'** are two similar bars, M and N. The cell, H, is mounted in its thermostat and connected by suitable lead wires across **A'** and N, as indicated in the figure. The variable resistance box, R_1, is connected across **A** and M by means of heavy links dipping into mercury cups. A variable air condenser, C_1, of suitable capacitance for the measurements being made is also connected across **A** and M. Ordinarily we use two condensers in parallel—one having a total capacitance of about 1000 $\mu\mu$f. made by the General Radio Company, Type 239E, and the other a small condenser made in our shop with one stationary and one movable plate capable of very fine adjustment; but some of our cells are so good that the large condenser may be removed as the small condenser is ample.

The resistance box, R_1, can be adjusted to tenths of an ohm. As a rule we prefer to use cells of high cell constant and make measurements with 10,000 ohms or more in the cell and in such case a box adjustable to tenths of an ohm gives adequate precision. It may be necessary or desirable to measure resistance as low as 100 ohms, which requires a means of adjusting the resistance continuously with a means for measuring in thousandths of an ohm. For this purpose we mount a single turn of manganin wire on a cylinder, Q, with a sliding contact, B', which is the mid-point of the bridge. An auxiliary resistance, R_7, of the proper magnitude to bring the mid point of the resistance between M and N at the point marked 0 on the dial, is inserted between M and the slide wire. Then if the slider, B', is at 0 the resistance between M and B' is equal to the resistance between N and B' and if this is the position of balance the resistance of the cell can be read off directly from the box (assuming of course that $R_3 = R_4$). But if B′ must be moved along the scale to obtain a balance then resistance is being added to R_1 and subtracted from R_2 and by proper calibration the reading of **B'** on the scale can be added to the reading of the box R_1 to give the actual resistance of the cell. This makes the bridge direct reading even down to the thousandths of an ohm. Of course in actual use an additive calibration correction for imperfect adjustment of the coils in the resistance box to their nominal values will be necessary, but no cumbersome calculations by ratios are required as in the common type of slide wire bridge. The resistance in the sliding contact at **B'** is not in the bridge circuit but only in the telephone circuit where it does no harm. In our instrument each division of the scale representing 0.001 ohm had a length of a little more than 1 mm. The scale is extended below the zero to -0.050 ohm and beyond the 100 to $+0.150$ ohm for convenience. The resistance wire and sliding contact are mounted under the cover but the dial and scale are on top. This device has given entire satisfaction in use. The very slight inductance of this single turn of wire can do no harm because, unlike the bridge criticized above, it is in the reactive arms of the bridge where it partly compensates the unavoidable capacitance in the cell.

It is difficult to exaggerate the advantage of having the bridge direct reading. The actual saving in time required by the calculations is important but by no means the chief advantage. Of greater importance is the fact that the significance of measurements can be appreciated at the time the measurements are being made instead of an hour or a month afterward, when the calculations are completed and the results tabulated. This helps tremendously in gaining an insight into a complexity of several subtle and superimposed effects.

The sliding contact B between the ratio arms is connected to switch S_5, which can be thrown so as to connect B either to the amplifier and telephone or to a galvanometer. After passing through the telephone (or galvanometer) the current returns to the other pole of S_5 and hence to the middle of switch S_2 which can be thrown during measurements so as to connect with the sliding contact, **B'**, or during adjustment of ground so as to connect **B** with ground through the telephone (with **B'** entirely disconnected from anything). The amplifier is connected to the instrument by shielded lead wires which are attached to biding posts in the southwest corner. The galvanometer is connected to suitable binding posts in the southeast corner.

The adjustment of the sliding contact B so as to make R_3 equal to R_4 is accomplished as follows. Two extra coils of 1000 ohms each, which have been adjusted so as to make them very nearly equal, are connected across the gaps AM and **A'N**, respectively, and the slider, **B'**, is set at zero. Then the bridge is balanced by moving the slider, B, and the position of B on the scale noted. Next the two 1000-ohm coils are interchanged and the slider, **B**, moved to a new balance and this position noted. The mid-point between these two readings of B will be the true mid-point of the ratio arms. The slider, B, is then moved to the proper point and firmly clamped in place, thus making the ratio arms exactly equal. This adjustment requires only a few minutes and may be checked at frequent intervals to make sure that the coils R_3 and R_4 are not changing.

Then with B at its proper place heavy links having equal and negligible resistance are placed across AM and **A'N**. **B'** is now moved until the bridge is in balance, which gives the true mid-point between M and N. If the scale does not read zero the scale is loosened on its shaft by turning its set screw and moved to the proper point without moving the slider and then tightened again.

The scale was then marked at intervals of 0.01 ohm experimentally without assuming that the wire was uniform. A standard 10-ohm coil was placed across the gap AM and another 10-ohm coil and an adjustable shunt placed across the gap **A'N** and the shunt adjusted to give a balance with the slider **B'** set at zero. Then by placing a shunt of suitable magnitude (9990 ohms) across the standard 10-ohm coil the resistance of the combination was reduced by 0.01 ohm and the slider B' moved until the balance was restored, which made it possible to mark this point on the scale. In like manner by changing the shunt the successive increments of 0.01 ohm were marked on the scale. These graduations were then subdivided into 0.001-ohm divisions.

Acknowledgments

This very expensive research would not have been possible without grants from the Elizabeth Thompson Science Fund, the Bache Fund of the National Academy of Sciences and the Milton Fund of Harvard University, for which we express our gratitude. We are indebted to Professor G. W. Pierce, Director of the Cruft Laboratory, for making available to us a room in the Cruft Laboratory and for many facilities of that Laboratory. We also take pleasure in thanking Professor E. L. Chaffee and Professor R. F. Field of the Cruft Laboratory for their continued interest in our work and for helpful suggestions.

Summary

This paper, the first of a series on the measurement of the conductance of solutions, discusses the design of alternating current bridges and accessories, for this purpose.

1. The best source of the current is an audion tube oscillator adjustable to several frequencies, and adjustable in voltage.

2. A one- or two-stage audion tube amplifier should be used with the telephone, as the detector. The amplifier, supplemented by the other improvements, gives a sensitiveness of one part in a million.

3. The use of cells of high cell constant (length divided by cross section) is recommended so that the resistance to be measured will be high (10,000–30,000 ohms), thereby reducing polarization and heating effects in the cell.

4. All methods of grounding hitherto used are erroneous, as was proved by the fact that the position of balance may be changed by reversing the lead wires from the oscillator to the ends of the bridge. A new method of grounding which avoids this source of error has been invented and is described in detail.

5. Electromagnetic and electrostatic shielding of the bridge proper are not recommended, but shielding of the source of outside disturbances is preferable.

6. It is proved experimentally that the use of water in the thermostat and the grounding of the thermostat may result in serious errors due to three causes. The use of oil as a thermostat liquid is recommended instead.

7. The conditions of balance of the bridge are analyzed mathematically. The equation, $R_1R_4 = R_2R_3$, which is commonly but erroneously assumed to be valid in any balanced bridge, is valid only if the phase angles between the voltage and current are equal in two pairs of adjacent arms. Special care in design and construction is necessary to ensure that these conditions are satisfied.

8. It is demonstrated that with the usual type of helical slide wire

bridge serious errors may be made if the results are computed in accordance with the formula $R_1R_4 = R_2R_3$, owing to the inductance in the helix.

9. It is recommended that the ratio arms R_3 and R_4 be constructed so as to be as nearly as possible free from reactance and identical in resistance and construction. Means of accomplishing this are discussed.

10. Means of providing reactance in one arm of the bridge to balance the unavoidable reactance of the cell are discussed. Kohlrausch's device of using a condenser in parallel with the resistance box is recommended. The error due to the shunting effect of such a condenser is discussed and a formula for its calculation given. This error is negligible except under abnormal conditions.

11. The reactance balance is made significant for the study of cell design.

12. It is demonstrated experimentally that the resistance boxes available by purchase have alternating current errors in the upper ranges, that is, their effective resistance with alternating current of audio frequency is a function of the frequency and different from the direct current resistance. It is shown that coils are available in which these errors are negligible. The errors in the best of the available boxes are traced to two causes: (a) dielectric losses in the insulators, chiefly between the switch contacts but also in some cases in unnecessary insulation on the lead wires, and (b) dissipation of energy in appended coils not in use. Means for avoiding these errors have been devised.

13. The specifications of an ideal box are described in detail.

14. Two new resistance boxes superior to any on the market for this purpose were built and are described.

15. A new form of bridge designed in accordance with the above principles has been built and is described in detail. It has the following improvements over those commonly used:

(a) A new and correct method of grounding.

(b) Non-reactive ratio arms easily adjustable to exact equality of resistance.

(c) Fine adjustment of the resistance down to 0.001 ohm in the resistance arm instead of the ratio arms.

(d) The reactance balance is significant.

(e) The bridge is sensitive to one part in a million.

(f) It can be used with either direct current or alternating current and changed by merely throwing two switches.

(g) The bridge is direct reading.

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[CONTRIBUTION FROM THE PHYSIOLOGICAL CHEMISTRY LABORATORY, UNIVERSITY OF MINNESOTA]

THE DETERMINATION OF TRACES OF IODINE. I.

BY J. F. MCCLENDON

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Since iodine is one of the rarest chemical substances and is absolutely essential to the life of human beings and other mammals, the determination of traces of this element is of some chemical importance. According to the atomic disintegration theory of the origin of the elements, the usual method of expulsion of a helium nucleus has led to the superabundance of the elements of even atomic weight. Those of uneven atomic weight are relatively rare and iodine is one of the rarest. Its wide distribution supports the idea that it was formed in place. It is not abundant enough to be acted on by the ordinary geological concentrating forces; there are no iodine mines and only small deposits of silver iodide.

If sufficient iodide is present for weighing, it may be precipitated as palladous iodide (PdI_2) by the addition of palladous chloride to the acid solution. After standing for two days in a warm place the precipitate will be coarse enough to filter through a Gooch crucible. It may then be washed with warm water, dried at 100° and weighed. Although Stieglitz[1] uses this reaction for microchemical detection of iodine in tissues, he does not use the balance; in fact, the sample is usually too small for gravimetric determination.

Iodide or iodine may be quantitatively oxidized to iodate by the action of bromine (as in Kendall's[2] method) or chlorine. The excess of bromine or chlorine may be boiled out. On the addition of an excess of potassium iodide, six times as much iodine is formed as the total of the element that was originally present in the sample. In the titration of iodine, starch is a sensitive indicator when iodide is also present. (Starch solution has reducing action only at elevated temperature.) The addition of iodide in the iodate method or to increase the sensitivity of the starch iodide reaction, necessitates the removal of all oxidizing agents which would liberate iodine from iodide. The oxygen of the air will liberate iodine from iodide, particularly in sunlight or in the presence of catalysts such as iron or other heavy metals. The heavy metals may be almost completely removed, even in acid solution, by the addition of phosphoric acid and filtration.

It may seem safer to analyze samples for the first time without the addition of iodide but, on the contrary, by the use of reagents which have

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[1] Stieglitz, *J. Pharmacol.*, **22**, 89 (1923).

[2] Kendall, *J. Biol. Chem.*, **43**, 149 (1920).

been carefully freed from iodine by recrystallization or distillation over alkali. Potassium salts and bromine are more likely to contain traces of iodine than sodium salts and chlorine. Nitric acid made from Chilean saltpeter is more liable to contain iodine than nitric acid made from the air. According to my own observations and those of Gautier, all the iodine in the atmosphere is in the farm of dust.

In the oxidation of iodide to iodine, careful selection of the oxidizing agent and control of the conditions are necessary in order to prevent the oxidation from proceeding too far (formation of iodate). Iodide may be oxidized to iodine by permanganate or by the action of nitrous acid in slightly acid solution, with simultaneous production of nitric oxide. In a moderate concentration of hydrogen ions the formation of nitric acid would be very small and would be retarded by preventing the escape of nitric oxide. If oxygen is present, some of the nitric oxide will be reoxidized to nitrous acid. The production of nitrogen gas is very slow and may be neglected. The iodine may be determined by the extraction method introduced by Rabourdin in 1850. If a water solution of iodine is shaken with an equal volume of carbon tetrachloride, about $^{85}/_{86}$ of the iodine passes into the carbon tetrachloride. If the water is 10 times the volume of the carbon tetrachloride, about $^{85}/_{95}$ of the iodine passes into the latter. If sulfates or nitrates are added to the water, more of the iodine passes into the carbon tetrachloride but if chlorides are added to the water, less of the iodine passes into the carbon tetrachloride. This effect is still greater with bromides but fortunately they are never in very high concentration. Iodides do not interfere in this form of analysis because all of the iodide is oxidized to iodine and hence none is present as iodide in the water solution. It is very desirable to reduce the concentration of chlorides and this may be accomplished by evaporating the solution to dryness and extracting it with absolute alcohol, which dissolves the iodide but very little of the chloride.

In the presence of organic substances of high molecular weight, the above methods of analysis of iodine fail. Even drinking water or sea water may contain too much organic matter for iodine analysis. Organic matter is usually destroyed by ashing but ashing in open dishes is often attended by loss of iodine even in the presence of alkali. It is for this reason that the method given below has been elaborated.

Procedure

In a previous paper,[3] some parts of the procedure were given and some improvements were indicated in a later note,[4] whereas the theoretical considerations and literature were given in a review.[5] More experience has since been gained in the determina-

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[3] McClendon, *J. Biol. Chem.*, 60, 289 (1924).

[4] McClendon, *Proc. Soc. Exptl. Biol. Med.*, 23,494 (1926).

[5] McClendon, *Physiol. Rev.*, 7, 240 (1927).

tion of traces of iodine, the method somewhat improved and simplified, and iodine analyses made of drinking water, sewage, cereal grains, vegetables, fruits, milk, butter, fish, mammalian tissues, urine, feces and other substances. In the ashing, the samples were burned in a large silica combustion tube open at one end. To avoid loss due to air currents at the opening of the tube, an attempt was made to close it partially with a sheet iron door but this was later replaced by an ordinary tinned funnel which served as a door and also for admission of oxygen. When oils were burned in the tube, it was found desirable to spray them in continuously. An apparatus was made for injecting powdered samples of foodstuffs in a similar manner, but if the combustion tube was only moderately heated, some particles of dust escaped combustion and when it was heated to a high temperature, the dust adhered to the automatic feed and clogged it. An automatic stoker in the form of a moving grate was next tried but it was found desirable to remove the automatic mechanism and move it continuously by hand.

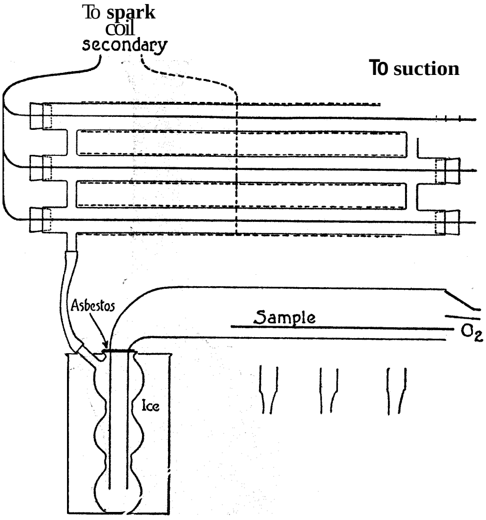

Fig. 1.

An atomizer for spraying in melted butter and an apparatus for feeding in milk powder will be described in a second paper.

The apparatus is shown in Fig. 1 and consists of a fused silica tube of 9 cm. bore and 60 cm. long with an elbow of 2.5 cm. bore and 30 cm. long, bent down into a Pyrex absorption flask containing 500 cc. of distilled water, to which 0.1 g. of sodium hydroxide has been added, and immersed in ice water. The neck of the flask is made air tight around the elbow by means of wet asbestos fibers. There is a side neck to the absorption flask leading to the Cottrell precipitator, which consists of 3 lead-glass tubes, 90 cm. long and 2.5 cm. bore, connected together in parallel by side necks (1.25 cm. bore) near each end. The tubes are closed with rubber stoppers through the centers of which run fine nichrome wires extending through the centers of the tubes and connected to one pole of the secondary of a Ford spark coil. The other pole of the spark coil is connected by means of a copper wire to tin foil covering the tubes. The spark coil is operated by a 6-volt storage battery and builds up a very high potential in one direction. By means of the side necks, one end of the Cottrell precipitor is connected with the absorption flask and the other end through 2 (or more) wash bottles (not shown in the figure) with a rotary suction pump. Each wash bottle contains 100 cc. of distilled water to which is added 0.02 g. of sodium hydroxide.

The open end of the silica tube is closed with a tinned funnel, admitting oxygen from a cylinder, and the lower edge of the funnel is bent up so that the sample may be introduced. The pump is run at its maximum rate and the oxygen is introduced as rapidly as possible without loss from the open end of the silica tube. The sample (of foodstuff, for instance) is placed on a piece of sheet iron, 6 cm. wide and 76 cm. long, which is introduced into the heated silica tube at such a rate that it burns completely in the oxygen (without soot or tar formation). If soot is formed the analysis is not ruined but the apparatus must be washed out and the washings evaporated and burned again. In order to prevent an explosion the sample is lighted with a gas pilot flame at the moment of introduction. In order to prevent the sample from burning outside the tube it is placed in separate piles on the sheet iron; and if all cannot be placed on one piece, the rest is placed on other pieces of sheet iron which are introduced in succession until the whole sample is burned. The heat applied to the outside of the silica tube must be very high in order to complete the burning of all the carbon, and is conveniently supplied from a row of large Méker burners. An asbestos roof over the tube is used to decrease the loss of heat. The Cottrell precipitator is useful in precipitating fine particles of ash that would not be caught by the wash bottles.

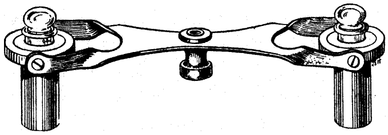

Fig. 2.

At the end of the ashing, the ash is removed to a ball mill and water is used in rinsing the sheet iron "boats," the Cottrell precipitator and silica tube, and this, together with the sodium hydroxide solution in the absorption flask and wash bottles, is evaporated to a small volume (2–5 cc.) and analyzed for iodine.

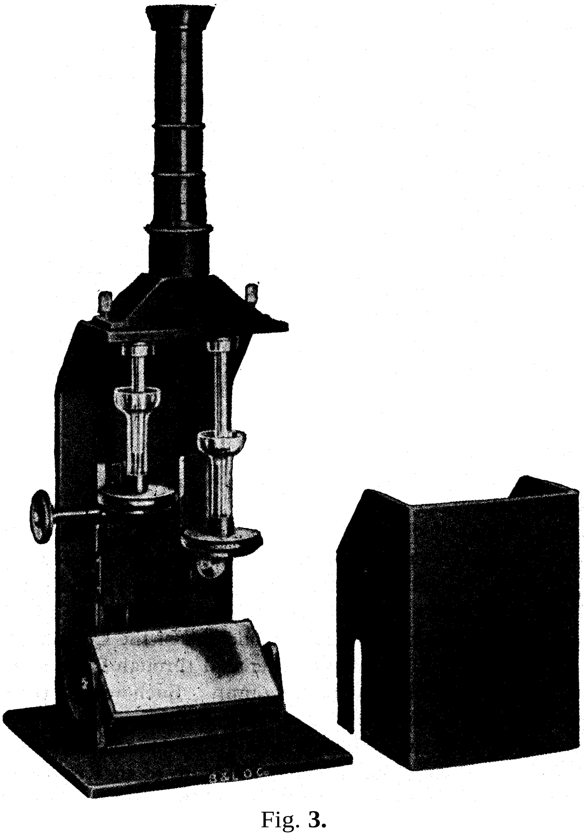

Fig. 3.

The ash is extracted with water or if it contains a large amount of water soluble salts with absolute alcohol (free from aldehyde) in a ball mill. Sufficient alcohol is used to permit decantation after the extraction, and the extraction is repeated several times. The combined extracts are filtered and evaporated. The residue is dissolved in about

2 cc. of water and analyzed separately or after addition to the sodium hydroxide solution and washings.

In the iodine analysis, the solution is neutralized with phosphoric acid (to which $^1/_5$ volume of 0.1 *N* sulfurous acid has been added) using an indicator paper made by drying an alcoholic solution of methyl orange or brom-phenol blue on ash-free filter paper. It is heated to boiling to expel carbon dioxide and sulfur dioxide and cooled. The volume is now made up to 10 cc. and the solution transferred to a 12cc. separatory funnel (preferably with a 10 cc. graduation mark for making up to volume). One cc. of purified carbon tetrachloride and 1 or 2 mg. of sodium nitrite are added and the separatory funnel is shaken 100 times; during the shaking $^{85}/_{95}$ of the iodine should pass into the carbon tetrachloride and color it pink or violet, so that by multiplying the yield by 1.118 the total iodine in the sample may be calculated. The carbon tetrachloride is cloudy with water droplets and is run into a 1cc. glass-stoppered bottle and centrifuged in the special centrifuge head shown in Fig. 2. It is then run into the left cup of the Bausch and Lomb micro-colorimeter shown in Fig. 3 and set at 20 mm. Carbon tetrachloride containing pure iodine of the concentration 0.1 mg. per cc. is placed in the right cup and a color match made. Ten readings are made and their average is taken. The reading in millimeters divided by 200 and multiplied by 1.118 gives the milligrams of iodine.

It is well for each person using the method to check his technic in the extraction of the iodine by taking 10 cc. of distilled water containing 0.1 mg. of iodine in the form of iodide in the separatory funnel, adding phosphoric acid to the turning point of the indicator paper, a small crystal of sodium nitrite and 1 cc. of carbon tetrachloride, and shaking 100 times. In analyses in which there is more than 2 mg. of iodine it will precipitate in the water and delay extraction and if the amount of iodine is very large its solubility in carbon tetrachloride may be a factor limiting extraction so that a series of repeated extractions is necessary. In this case the iodine in each extraction is determined separately in the colorimeter and the amount in the last extraction only multiplied by 1.118. Then the various amounts are added together to obtain the total.

In the analysis of drinking water much time may be saved by adding sodium carbonate and filtering out the alkaline earths during the evaporation. Only 2% of the iodine is lost by filtering a 100-liter sample boiled down to 1 liter (after adding 1 g. of sodium carbonate). Some organic matter is carried down in the precipitate and probably holds tenaciously some of the iodine. Although the iodine content of the sludge of sewage purification plants is much higher than that in the run-off (on the basis of the same water content), showing that the iodine is concentrated in the organic precipitate (in the bodies of live bacteria or dead material), in the case of drinking water the amount of organic matter is very much less, in fact comparatively insignificant, and the loss due to filtering off some of the organic matter is negligible. The organic matter remaining in drinking water after boiling and filtering is usually so low that a smaller tube (of Pyrex glass) may be used in the combustion and the precipitator dispensed with.

In the case of soils, combustion in the tube is desirable before proceeding with the analysis, and the hydrochloric acid-soluble portion may be analyzed according to the procedure outlined above. The biological significance of the analysis of the hydrochloric acid-insoluble portion (fused with sodium hydroxide) is not apparent as it is doubtful if it is available to organisms.

An average of 10 readings with the Duboscq colorimeter is about as accurate as one reading on a buret and there is no occasion for verifying the colorimetric determination by means of subsequent titration, as done by Von Fellenberg.[6]

Technical carbon tetrachloride may be used in the analysis if oxidized with chlorine or bromine in sunlight, washed with sodium hydroxide solution and water, dried with plaster of Paris, and distilled, rejecting the cloudy portion of the distillate.

If any ash that comes in contact with the hot silica tube is removed with hydrofluoric acid before the tube is used again, its life will be prolonged. It might be economical to use a smaller tube. The rate of combustion is limited by the size of the pump and precipitator. The original tubes were 4 ft. long and were found to be too large.

Since 0.001 mg. is about the limit of iodine that may be determined in the micro-colorimeter, it is necessary to have more than 0.01 mg. for accurate work. The iodine content of many samples of foodstuffs is so low that it may be necessary to burn several kilos in one analysis. The absolute accuracy in such extreme cases is somewhat doubtful, but the general value of the method is attested by the following results. Starch was purified until no iodine could be detected in it by the method, then to a 50-gram sample was added a known quantity of iodine in the form of a potassium iodide solution. The results were as follows.

IODINE IN MILLIGRAMS

	1	2	3
Added..............	0.045	0.20	0.090
By analysis..........	**.046**	.19	**.093**

In order to show the relative value of the different features of the combustion method, a much larger sample of iodide was added to starch and the ash and various fractions of volatilized iodide were analyzed separately with the following results.

	Total iodine added to starch, %
Ash.........................	44.4
Large absorption flask............	47.0
Precipitator.....................	5.7
1st wash bottle..................	1.4
2nd **wash** bottle.................	0.7
Total recovered.............	99.2

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[6] Von Fellenberg, *Biochem.* Z., 152, 116 (1924).

In the above experiment the silica tube was heated only sufficiently to burn the sample, but when it is heated to a high temperature, the iodide is sometimes completely volatilized, none remaining in the ash. In case the ash is bulky and alkaline, it retains more of the iodine. In burning thyroids some of the iodine appeared to sublime as I_2 and it is suggested that in case organic matter does not reduce all of the iodine to iodide, a little sulfur be added to the sample.

Although the errors by this method may be 1% on samples containing more than 1 mg. of iodine and 5% on samples containing less than 1 mg. of iodine, it was shown by McClendon and Rask[7] that the method of Kendall, which is accurate for 0.5 g. of thyroid or 100 g. of blood, entirely fails in the analysis of iodine in Minnesota wheat, some samples of which contain only 1 mg. of iodine per metric ton of wheat (McClendon and Hathaway).[8] Attempts were made to compare the method with that of Von Fellenberg but I did not acquire sufficient skill with his method to be confident of the results. Since his colorimetric determinations are made under the microscope, special skill is required.

Some refinements of technique were worked out in collaboration with Gertrude Humphrey Beckwith[9] in relation to her work on the iodine content of water supplies. Appreciation is due to Don R. Mathieson for assistance in some of the experiments and to the American Medical Association for a grant for purchasing some of the apparatus.

Summary

Traces of iodine are determined colorimetrically in a micro-colorimeter made on the Duboscq principle. If organic matter is present in the sample it is burned in oxygen in a tube and the combustion products are sucked through sodium hydroxide solution and a Cottrell precipitator. The limit of error is 1% on samples containing more than 1 mg. of iodine and 5% on samples containing less than 1 mg. A sample of foodstuff as large as several kilograms can be used in one determination; hence the process is possible where most other methods entirely fail.

MINNEAPOLIS, MINNESOTA

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[7] McClendon and Rask, *Proc. Soc. Exptl. Biol. Med.*, *20*, 101 (1922).

[8] McClendon and Hathaway, *J. Am. Med. Assocn.*, 82, 1668 (1924).

[9] Beckwith, *Proc. Soc. Exptl. Biol. Med.*, 25, 117 (1927).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 198]

THE EQUATION OF STATE FOR BINARY MIXTURES OF METHANE AND NITROGEN

BY FREDERICK G. KEYES AND HARRY G. BURKS

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Introduction

The experimental work here reported was carried out during the years 1923 and 1924 for the purpose of ascertaining whether or not the equation of state which represented the separate gases, nitrogen and methane, was also capable of representing the data for mixtures of the two gases. The measurements have been found to give an affirmative answer and in addition yield the interesting result that the constants of equations of state for the mixtures are linear functions of the constants for the pure gases and the compositions of the mixtures. More explicitly, the β, α, and l constants for the mixtures appear to be given within a reasonably good approximation by the equations $\beta_{N_2}W_{N_2} + \beta_{CH_4}W_{CH_4}$, $\alpha_{N_2}W_{N_2} + \alpha_{CH_4}W_{CH_4}$, $l_{N_2}W_{N_2} + l_{CH_4}W_{CH_4}$ where the β_{N_2}, β_{CH_4}, etc., represent constants for the separate components and the Ws refer to the masses of the constituents. The A constant is of the same form in the square root of the constants of the separate gases, namely, $(\sqrt{A}_{N_2}W_{N_2} + \sqrt{A}_{CH_4}W_{CH_4})^2$.

The stated relation between the constants of the separate gases and the composition has been obtained by neglecting the "curvature" of the isometrics. Actually this introduces relatively only a small error in computing the *pressures* since the departure of the gaseous mixtures from isometric linearity is small in the region of 0 to 200°. It is of course possible to allow for the isometric curvature in the manner already used for N_2,[1] CO_2,[2] CH_4[3] and $(C_2H_5)_2O$.[4] The detailed consequences for the additive rule of constants when allowance is made for the isometric curvature will be presented in a later paper.

It will be clear that the additive rule is a further step in the direction of providing a basis for the development of a more general mass action expression for chemical reactions in the gaseous phase. Already, in fact, Lewis and Gillespie[5] have applied the rule to their data on ammonia–nitrogen mixtures. Keyes[6] has also used the above additive equation of state constants rule to compute the Haber equilibrium to 1000 atmospheres

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[1] Keyes and Taylor, THIS JOURNAL, 49, 896 (1927).

[2] Bridgeman, *ibid.*, 49, 1130 (1927).

[3] Keyes and Burks, *ibid.*, 49, 1403 (1927).

[4] Beattie, ibid., 49, 1123 (1927).

[5] Lewis and Gillespie, *ibid.*, 47, 305 (1925); 48, 28 (1926); 49, 1146 (1927).

[6] Keyes, *ibid.*, 49, 1393 (1927).

in a somewhat different manner (and, all things considered, a tolerable agreement with the observational material for the equilibrium results).

The choice of gases for the present investigation depends among other things upon the chemical indifference of methane in the presence of nitrogen. Both gases were, moreover, in the experimental temperature range of the apparatus available, well above their respective critical temperatures—a matter of importance from the point of simplicity of interpretation because of the nearly linear character of the isometrics at higher temperatures. The gases are, moreover, both of the non-polar type. The quality of the gases employed was similar in every way to the gases employed for the measurements of pure methane and nitrogen.? It is of interest to note also that not only were the gases for the "mixtures" measurements made with gases of identical quality as those used to obtain the constants for the pure gases but the same apparatus was used alike for pure gases and mixtures. The consistency of the data as a whole should accordingly be favored.

The Experimental Data

Tables I, II and III give the data for three mixtures, two of which are nearly of the same composition. The first row in each table records the

TABLE I

PRESSURE, VOLUME, TEMPERATURE DATA POR THE NITROGEN–METHANE MIXTURE 0.6956 G. OF NITROGEN—0.3044 G. OF METHANE

Pressure in International atmospheres; volumes in cc. per g.

Volume, cc./g.	0°	50°	100°	150°	200°	
30	31.640	38.172	44.664	51.126	57.591	**Obs.**
	31.664	38.149	44.635	51.120	57.606	**Calcd.**
25	37.756	45.711	53.634	61.513	69.381	**Obs.**
	37.782	45.688	53.594	61.500	69.406	**Calcd.**
20	46.812	56.998	67.146	77.220	87.281	**Obs.**
	46.855	56.972	67.089	77.206	87.323	**Calcd.**
15	61.681	75.810	89.886	103.823	117.737	**Obs.**
	61.759	75.783	89.807	103.831	117.855	**Calcd.**
12	76.349	94.723	113.010	131.113	149.225	**Obs.**
	76.476	94.694	112.912	131.130	149.348	**Calcd.**
10	90.952	113.864	136.643	159.246	181.658	**Obs.**
	91.101	113.811	136.521	159.231	181.941	**Calcd.**
8	112.929	143.254	173.483	203.305	233.066	**Obs.**
	113.088	143.121	173.153	203.186	233.218	**Calcd.**
6	150.927	195.529	239.853	283.615	327.443	**Obs.**
	150.575	194.448	238.321	282.194	326.067	**Calcd.**

$$p^{\text{atm.}} = \frac{3.5950}{v - \delta}T - \frac{3434.9}{(v + 0.2094)^2}$$

$$\log_{10}\delta = 0.37861 - \frac{0.5951}{v}$$

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[7] Smith and Taylor, THIS JOURNAL, 45,2107 (1923); 48, 3122 (1926).

TABLE II

PRESSURE, VOLUME, TEMPERATURE DATA FOR THE NITROGEN–METHANE MIXTURE 0.3101 G. OF NITROGEN—0.6899 G. OR METHANE

Pressure in International atmospheres; volumes in cc. per g.

Specific volume	0°	50°	100°	150°	200°	
29.946	37.700	45.994	54.227	62.424	70.592	Obs.
	37.682	45.894	54.107	62.319	70.532	Calcd.
24.946	44.662	54.814	65.036	74.920	84.913	Obs.
	44.665	54.723	64.781	74.839	84.897	Calcd.
19.946	54.823	67.948	80.918	93.821	106.684	Obs.
	54.868	67.826	80.784	93.742	106.700	Calcd.
14.946	71.113	89.484	107.710	125.792	143.701	Obs.
	71.275	89.426	107.577	125.728	143.879	Calcd.
11.946	86.974	110.899	134.726	158.570	182.031	Obs.
	87.102	110.905	134.708	158.511	182.314	Calcd.
9.946	102.359	132.464	162.645	192.505	222.069	Obs.
	102.531	132.451	162.371	192.291	222.211	Calcd.

$$p^{\text{atm.}} = \frac{4.4383}{v - \delta}T - \frac{6660.4}{(v + 0.5113)^2}$$

$$\log_{10} \delta = 0.49721 - \frac{0.937}{v}$$

TABLE III

PRESSURE, VOLUME, TEMPERATURE DATA FOR THE NITROGEN–METHANE MIXTURE, 0.2969 G. OF NITROGEN—0.7031 G. OR METHANE

Pressure in International atmospheres; volumes in cc. per g.

Volume, cc./g.	0°	50°	100°	150°	200°	
40	28.868	34.972	41.038	47.075	53.084	Obs.
	28.900	34.954	41.008	47.062	53.115	Calcd.
35	32.750	39.811	46.821	53.803	60.738	Obs.
	32.790	39.787	46.784	53.781	60.778	Calcd.
30	37.843	46.220	54.514	62.773	70.988	Obs.
	37.898	46.183	54.469	62.754	71.040	Calcd.
25	44.819	55.089	65.260	75.360	85.414	Obs.
	44.898	55.048	65.198	75.348	85.498	Calcd.
20	55.002	68.262	81.353	94.371	107.308	Obs.
	55.098	68.178	81.258	94.338	107.418	Calcd.
15	71.298	89.910	108.283	126.483	144.608	Obs.
	71.393	89.715	108.037	126.359	144.681	Calcd.
12	87.008	111.450	135.606	159.515	183.313	Obs.
	86.935	110.951	134.967	158.982	182.998	Calcd.
10	102.360	133.203	163.655	193.779	223.800	Obs.
	103.042	133.200	163.360	193.519	223.677	Calcd.

$$p^{\text{atm.}} = \frac{4.46475}{v - \delta}T - \frac{6803.6}{(v + 0.4)^2}$$

$$\log_{10} \delta = 0.51760 - \frac{1.0371}{v}$$

observed pressures and the row immediately beneath the pressures computed by the respective equations (based directly on the data) placed at the bottom of each table. The isometrics are not strictly linear for the mixtures. For the pure gases the isometrics of nitrogen show very little curvature in the temperature region 0–200°, while the methane isometrics show pronounced enough curvature to be treated quantitatively.[3] The isometrics of the mixtures show less curvature as the amount of methane diminishes, as would perhaps be expected. The pressures evidently are well represented by the equations, which are of the same general form as may be used for representing the pressures of the pure gases.

Figs. 1 and 2 give a survey of the additive volumes rule[8] (Leduc's rule) and the additive pressures rule (Dalton's rule).[9] The even pressures for Fig. 1 were obtained by graphical treatment, while Fig. 2 contains the observational material taken directly from Tables I and III. It is quite evident that the agreement of these computed volumes or pressures does not accord with the observed volumes or pressures. It is to be noted, however, that the additive volumes relation gives better accord with the experimental data than the additive pressures. For both additive relations the agreement improves as higher temperatures are approached. In every instance also the observed volumes for constant pressures and the

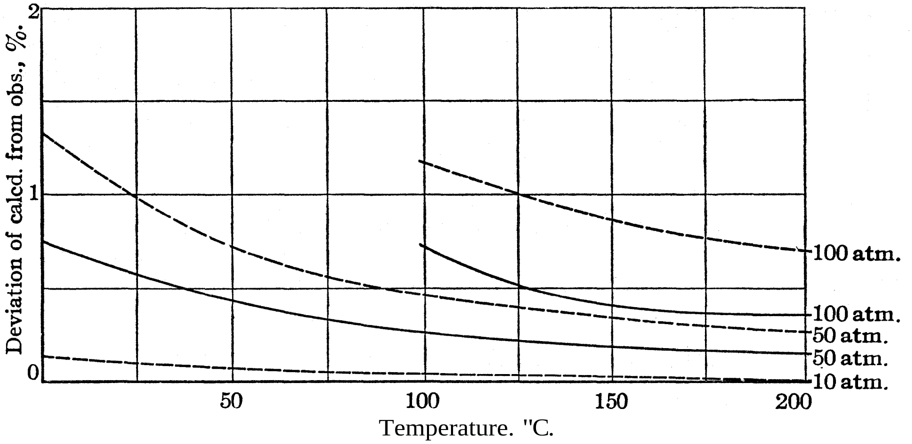

Fig. 1.—The calculated numbers are obtained from the formulas $v_{\text{calcd.}} = 0.3044 v_{CH_4} + 0.6956 v_{N_2}$ and $v_{\text{calcd.}} = 0.7031 v_{CH_4} + 0.2969 v_{N_2}$, where v_{CH_4} and v_{N_2} are the volumes of the pure gases under the same pressure and temperature as the mixture. The ordinates are the percentage differences between observed and "calculated" or $[(v_{\text{obs.}} - v_{\text{calcd.}})/v_{\text{obs.}}] \times 100$.

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[8] The "calculated" volumes (cc. per g. of mixture) are obtained by using the measured or experimental volumes for methane and nitrogen, v_{CH_4}, v_{N_2}, in the formula $v_{\text{calcd.}} = v_{CH_4} 0.3044 + v_{N_2} 0.6956$.

[9] The "calculated" pressures (atm. for volumes in cc./g.) are obtained by using the measured or experimental pressures for methane and nitrogen, p_{CH_4}, p_{N_2}, in the formula $p_{\text{calcd}} = p_{CH_4} 0.30444 + p_{N_2} 0.69555$.

observed pressures for constant volumes are greater than those computed by these rules.

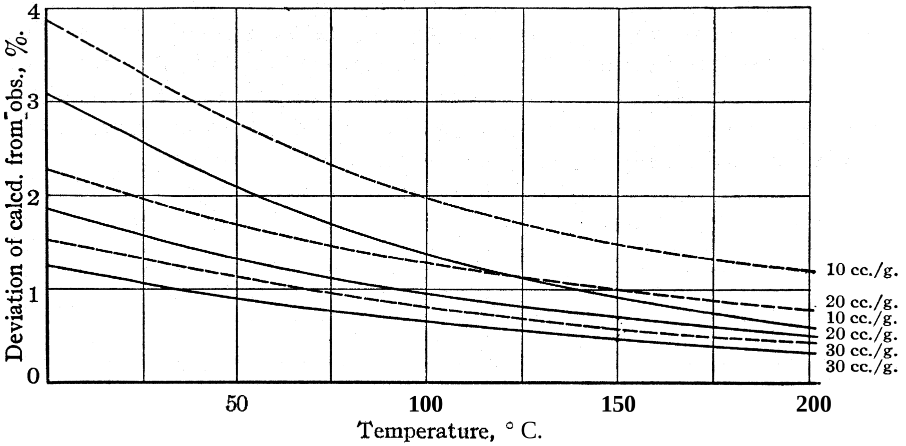

Fig. 2.—The calculated numbers are obtained from the formulas $p_{calcd.} = 0.3044\, p_{CH_4} + 0.6956\, p_{N_2}$ and $p_{calcd.} = 0.741\, p_{CH_4} + 0.2969\, p_{N_2}$, where p_{CH_4} and p_{N_2} are the pressures of the pure gases under the same volume and temperature as the mixture. The ordinates are the percentage differences between observed and "calculated" or $[(p_{obs.} - p_{calcd.})/p_{obs.}] \times 100$.

Relations between the Equation of State Constants

Table IV contains the equation of state constants for pure nitrogen in the second column and those for methane in the third column. The remaining columns contain the constants for the mixtures noted at the top of each column. The horizontal rows of constants marked "calcd." are computed using the following linear relations between the constants for the pure gases and the composition of the mixtures where the W's are the weights of gases composing a gram of mixture. The constants given in the table for pure methane, it should be stated, are those obtained by ignoring the curvature of the isometrics of methane. It is clear that

TABLE IV

CONSTANTS FOR EQUATIONS FOR PURE GASES AND MIXTURES

Units: cc. per g. International atmospheres

	N_2	CH_4	CH_4, 70.31%	CH_4, 68.99%	CH_4, 30.44%
$A_{obs.}$	1650.5	10151.4	6803.6	6660.4	3434.9
$A_{calcd.}$	....	....	6872.8	6741.8	3472.6
$\beta_{obs.}$	1.65	3.961	3.293	3.142	2.391
$\beta_{calcd.}$	....	....	3.275	3.245	2.354
$\alpha_{obs.}$	0.992	2.857	2.388	2.158	1.370
$\alpha_{calcd.}$	....	....	2.304	2.279	1.560
$l_{obs.}$	0.313	0.536	0.400	0.511	0.209
$l_{calcd.}$	....	....	0.470	0.467	0.381
R	2.9286	5.1173	4.4675	4.4383	3.5950

very good agreement obtains between the "synthetic" constants and those determined directly from the observational data. Tables V and VI give a sufficient survey of the accuracy with which the equations of state computed from the constants of the pure gases for two of the mixtures give the pressures of the mixtures compared with the observed pressures.

TABLE V

PRESSURES FOR THE 30 44 WEIGHT PER CENT. METHANE MIXTURE COMPUTED WITH THE "SYNTHETIC" EQUATION OF STATE AND COMPARED WITH THE MEASURED PRESSURES

Volume, cc./g.	0°	50°	100°	150°	200°	
30	31.603	38.077	44.551	51.025	57.499	Calcd.
	31.640	38.172	44.664	51.126	57.591	Obs.
20	46.732	56 817	66.902	76.987	87.073	Calcd.
	46.812	56.998	67.146	77.220	87.281	Obs.

$$p^{\text{atm.}} = \frac{3.5950}{v - \delta}T - \frac{3472.6}{(v + 0.381)^2}$$

$$\log_{10}\delta = 0.37181 - \frac{0.678}{v}$$

TABLE VI

PRESSURES FOR THE 70.31 WEIGHT PER CENT. METHANE MIXTURE COMPUTED WITH THE "SYNTHETIC" EQUATION OR STATE AND COMPARED WITH THE MEASURED PRESSURES

Volume, cc /g.	0°	50°	100°	150°	200°	
30	37.846	46.130	54.413	62.697	70.980	Calcd.
	37.843	46.220	54.514	62.773	70.988	Obs.
20	55.029	68.106	81.183	94.259	107.336	Calcd.
	55.002	68.262	81.353	94.371	107.308	Obs.

$$p^{\text{atm.}} = \frac{4.4675}{V - \delta}T - \frac{6872.8}{(v + 0.47)^2}$$

$$\log_{10}\delta = 0.51521 - \frac{1.00}{v}$$

This is the first time within the knowledge of the writers that information has been obtained by direct experiment concerning the combination rule of the constants of the equations of state of mixtures (in terms of the constants and masses of the constituent gases). The scheme (1) has, however, been used by van der Waals and others.

$$\begin{aligned} A &= (\sqrt{A}_{N_2}W_{N_1} + \sqrt{A}_{CH_4}W_{CH_4})^2 \\ \beta &= \beta_{N_2}W_{N_2} + \beta_{CH_4}W_{CH_4} \\ \alpha &= \alpha_{N_2}W_{N_2} + \alpha_{CH_4}W_{CH_4} \\ l &= l_{N_2}W_{N_2} + l_{CH_4}W_{CH_4} \end{aligned} \tag{1}$$

It is quite possible that the combination scheme will be less simple for molecules whose "diameters" are less nearly equal than is the case for nitrogen and methane. Attention should be called in the case of these mixtures to the fact that the interaction constant of van der Waals for these nitrogen–methane mixtures has been successfully represented by the relation $A_{12} = \sqrt{A_{N_2}A_{CH_4}}$. In a later paper the theoretical conditions under which this can be true will be discussed.

Summary

1. Experimental data for three mixtures of nitrogen and methane have been obtained for the temperature range 0 to 200° and to pressures amounting to 200 or 300 atmospheres.

2. The equation of state for each mixture has been found to be the same in form as that applying to the pure gases.

3. The constants of the equations of state representing the mixtures were found to be linear functions of the constants of nitrogen and methane and compositions of the mixtures as follows: $A = (\sqrt{A}_{N_2}W_{N_2} + \sqrt{A}_{CH_4}W_{CH_4})^2$; $\beta = \beta_{N_2}W_{N_2} + \beta_{CH_4}W_{CH_4}$; $\alpha = \alpha_{N_2}W_{N_2} + \alpha_{CH_4}W_{CH_4}$; $l = l_{N_2}W_{N_2} + l_{CH_4}W_{CH_4}$.

4. The generalized equation of state based on the present results for a mixture of n gases would be written

$$p = \frac{\Sigma R_1 W_1 T}{v - \Sigma\beta_1 W_1 e^{-\frac{\Sigma\alpha_1 W_1}{v}}} - \frac{(\Sigma\sqrt{A}_1 W_1)^2}{(v + \Sigma l_1 W_1)^2}.$$

CAMBRIDGE, MASSACHUSETTS

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

EQUILIBRIUM IN THE REACTIONS OF TIN WITH WATER VAPOR AND CARBON DIOXIDE

BY E. D. EASTMAN AND PRESTON ROBINSON

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The reactions of metals and their oxides with water vapor, together with the corresponding reactions with carbon dioxide, offer an indirect method of study of the water–gas equilibrium. Conversely, the equilibrium data pertaining to the latter reaction may be used to test the consistency of results obtained in the systems involving the metals. A series of such inter-comparisons in the case of iron and its oxides[1] revealed a large difference between the directly and indirectly determined values of the water–gas equilibrium constant. In view of the close agreement of the two sets of indirect determinations with each other it appears probable that the directly obtained data are in error. It remains desirable, however, to test this conclusion by further experiments. With that object the work here described was undertaken.

The equilibria selected for study may be represented by the following equations

$$Sn(l) + 2H_2O(g) = SnO_2(s) + 2H_2;\ K_1 = (H_2)/(H_2O) \qquad (1)$$

$$Sn(l) + 2CO_2 = SnO_2(s) + 2CO;\ K_2 = (CO)/(CO_2) \qquad (2)$$

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[1] Eastman *and Evans,* THIS JOURNAL, *46,888* (1924).

These equations may, of course, be combined to give that for the water–gas reaction, which will be written

$$H_2 + CO_2 = H_2O + CO;\ K_3 = (H_2O)(CO)/(H_2)(CO_2) = K_2/K_1 \qquad (3)$$

The systems shown in Equations 1 and 2 are well suited to the purpose stated. The gas phases at equilibrium in convenient temperature ranges contain readily measurable quantities of both constituents. The liquid tin is less subject to structural and surface differences than solid metals and may therefore be assumed to be nearly identical in character in the two systems. The stannic oxide necessary may be obtained (within the apparatus employed) by the reactions themselves, and should show little difference in character as prepared by the two very similar methods. That it is stannic oxide rather than stannous that is formed in these reactions is known from the work of Fraenkel and Snipischski[2] and Maeda.[3] They proved that SnO is unstable at the temperatures obtaining in our experiments. Finally, there is no evidence of solution to any appreciable extent of the condensed phases in each other, a point which is important only because of the possibility that solid solutions, which are known to be involved in the previous tests,' may be less readily reproducible as to state than nearly pure phases.

Measurements in Reaction 1

Dynamic Method.—The first method employed for the determination of K_1 was of the dynamic type. In principle it consists in finding the proportion of water vapor in a stream of it mixed with hydrogen that is just sufficient to produce continued oxidation when passed over tin held at a constant high temperature, the pressure being atmospheric.

In our application of this method the gas stream was obtained by passing hydrogen over distilled water in saturators immersed in a constant temperature bath. By changing the temperature of the thermostat the composition of the gas stream could be varied. The determination of its composition was made by measuring the temperature of the thermostat, the partial pressure of water vapor being taken as its vapor pressure at the measured temperature and that of hydrogen being obtained by subtraction of this value from the barometric pressure.

The tin, in the form of small drops, was contained in a long-necked bulb of silica glass held at nearly constant temperature in an electrically heated pot furnace. The neck of the flask projected from the furnace. It was fitted with an eyepiece of plane silica glass through which the tin in the bulb could be observed. On passing gas from the saturator through the flask it was readily determined from the appearance of the tin whether the gas was oxidizing or reducing in character. In an oxidizing atmosphere a white coating of oxide appeared on the tin; in reducing atmospheres this coating disappeared, or the tin remained bright. By successive settings of the thermostat it was possible to obtain a gas mixture of a composition such that slight variations in it would alternately oxidize the tin or reduce the oxide. This was taken as the composition of the mixture in equilibrium with the tin at the temperature of the interior of the flask. This

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[2] Fraenkel and Snipischski, *Z.* anorg. Chem., 125,235 (1922).

[3] Maeda, Bull. *Inst.* Phys. *Chem.* ***Research (Tokyo)*,2,350 (1923).**

temperature was measured by a thermocouple. Details concerning the experiments follow.

The hydrogen was generated by electrolysis of sodium hydroxide solution. The tin was a commercial preparation purporting to be of high purity.

The saturator consisted of a series of glass tubes about 4 cm. in diameter placed horizontally in the thermostat and half filled with water. The hydrogen passed over but did not bubble through the water.

The temperature of the thermostat was measured with a Beckmann thermometer which was compared with a thermometer calibrated by the Bureau of Standards. The gas compositions calculated from the measured temperature of the thermostat and the barometric pressure were checked by analysis at the two extremes of the composition range employed. Agreement was found to be within 1% in each case.

The gases from the saturator entered the neck of the flask near its top, and were preheated in the neck by a Chromel wire heater wrapped around it. From the neck the gases entered the bulb of the flask, where they were in contact with the tin, and escaped through a capillary the tip of which was under water. After resettings of the thermostat, a long interval with all conditions constant was allowed to ensure uniformity of composition of gas and give ample time for reaction with the tin.

Illumination of the interior of the bulb was accomplished by inserting a silica glass tube through the asbestos packing of the furnace to the wall of the bulb (at an angle of about 30° with the neck of the flask) and placing a 500-watt lamp at the outer end. At high temperatures the visibility of the tin was greatly diminished. Much above 800° the thermal radiation within the flask was so intense as to prevent distinct observation of the state of the tin.

The temperature of the furnace was regulated by hand. The thermocouple employed for measuring the temperature of the flask was of platinum and platinum-rhodium. It was calibrated against the melting point of various salts by the method of Roberts.[4] It was inserted during measurements in a protecting tube sealed through the wall of the bulb and extending nearly to its bottom. E.m.f.'s were read on a portable potentiometer to 0.01 mv. Temperatures determined with it we consider to be correct to within 5°.

A sample series of observations is shown in the following tabulation.

TABLE I

TYPICAL OBSERVATIONS

Barometric press., mm.	E.m.f. of thermocouple, mv.	Thermostat temp., °C.	Condition of tin
759.8	5.65	89.90	Reduced
753.6	5.65	90.20	Oxidized
752.7	5.60	90.00	Oxidized
749.7	5.65	89.95	Oxidized
751.6	5.68	89.85	Reduced
751.6	5.68	89.95	Oxidized
751.6	5.68	89.90	Reduced
754.0	5.69	90.05	Oxidized
751.6 ± 0.2	*5.68* ± 0.05	*89.92* ± 0.05	

The final (italicized) figures in each column are those chosen as representative of the equilibrium condition. Our estimate of the possible error in these values is also indicated. The vapor pressure of water

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[4] Roberts, Phys. *Rev.*, 23, 386 (1924).

at 89.92" was taken as 524.0, the error corresponding to the uncertainty in the temperature being about 1 mm. From this the value of K_1 is calculated to be 0.434 ± 0.004. The furnace temperature corresponding to 5.68 mv. is 655 ± 5°. The combined error in the temperature measurement and the constant itself should not exceed about 5% in individual determinations.

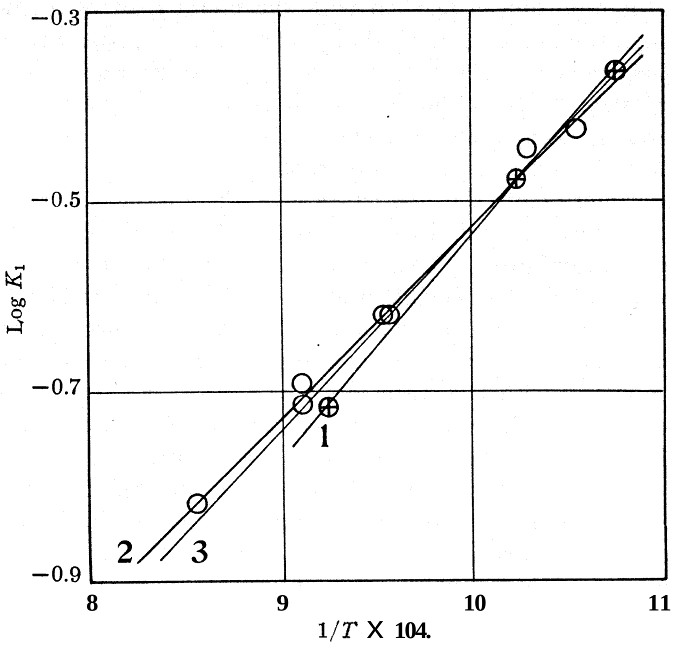

Fig. 1.—Equilibrium constant of reaction 1. Curve 1, Dynamic Method; Curve 2, Static Method; Curve 3, Best Values.

The final values obtained, each based on an extended series of observations similar to the preceding, are recorded in Table II and shown graphically in Curve 1 of Fig. 1.

TABLE II

EQUILIBRIUM CONSTANTS OF REACTION 1 FROM DYNAMIC MEASUREMENTS

t, °C.	655	703	809
K_1	0 434	0.333	0.191

Static Method.—Several considerations made it appear desirable to determine the value of K_1 by an independent method. The above modification of the dynamic method, while possessing many advantages and apparently free from large error, had never previously been used. Again, the coatings of stannic oxide produced in the reactions, while they were far from being merely surface films, did not contain large amounts, and the material need not be quite identical with "massive" samples. Finally, the values in Table II do not agree at all with the only previous measurements in this system, those of Wohler and Balz.[5] For these reasons measurements were made also by the well-known method of Deville.

The principle of this method, it will be recalled, is to allow water vapor from a reservoir maintained at a constant and known temperature to react until equilibrium is reached with the metal kept at a known and constant high temperature in another portion of the apparatus, the course of the reaction being followed by observing the pressure. The partial pressure of water vapor at equilibrium is taken as the vapor pressure of water at the measured temperature of the thermostat, and the partial pressure of hydrogen obtained by difference.

In these experiments the temperature of the thermostat ranged from 50 to 70°. It was measured to 0.02' with a thermometer calibrated by the Bureau of Standards. The thermostat was constant to 0.05° or better.

The tin, about 5 g. in weight, was contained in a porcelain boat in a silica glass tube in a tubular resistance furnace. The section containing the boat was 2.5 cm. in diameter and 10 cm. long. A tube 1 cm. in diameter connected with the water reservoir and a capillary tube at the opposite end led to the manometer and pump. The tube was pumped out and baked before runs. To insure the presence of a considerable amount of oxide a stream of water vapor was pumped over the tin for fifteen minutes at about 800° before starting any of the runs, and for shorter intervals between several of the runs. Determination of the vapor pressure of water within the apparatus while the furnace was at 200° agreed to 0.3 mm., about the error in pressure measurement, with the standard values at the measured temperature of the thermostat. The tube leading from furnace to reservoir was bent at an angle of 90° and again at 45°, so there was no direct radiation reaching the surface of the water from the furnace.

The thermocouple was enclosed in a thin-walled protecting tube sealed into the reaction chamber in a position just over the tin in the boat. Measurements with it are of about the same accuracy as in the preceding. The current for the furnace was drawn from storage batteries and remained sensibly constant over long periods of time, requiring little regulation of the furnace temperature once it was suitably set.

Pressures were read on an open-end mercury manometer of 5 mm. bore, provided with a leveling bulb so that the mercury column could be adjusted to a position close to the capillary opening, eliminating dead space. The capillary connecting tubes and a 10cm. length of mercury in the manometer were heated electrically to prevent condensation of water vapor. The temperature of the heated portion of mercury was

[5] Wohler and Balz, *Z. Elektrochem.*, 27, 406 (1921).

approximately measured by means of thermocouples, and density corrections made. The barometer and steel scale of the manometer were calibrated by comparison with a standard meter, with the aid of a cathetometer. Correction for capillarity was also made.

In some of the experiments the pressure was still slowly changing when the observations were discontinued, though the approach to equilibrium was always close. In these cases a small extrapolation to the final equilibrium condition was made by each of two methods. In the first, entirely empirical, the total pressure or its logarithm was plotted against the reciprocal of the time of observation and the series extrapolated to zero. The second method has a semi-theoretical basis. In the vicinity of the equilibrium conditions the rate of change of pressure may no doubt be assumed to be proportional to the distance from equilibrium, that is, to $p_0 - p$, where p is the pressure at a given time and p_0 the equilibrium pressure. If this is true it follows that a plot of log $(p_0 - p)$ against the time should be linear. Selecting by trial values of p_0 such that this is fulfilled gives the desired limiting figure. These two methods of extrapolation agreed well.

The directly observed quantities and final calculated results are shown in Table III, and the points corresponding are also plotted in Curve 2 of Fig. 1.

TABLE III

EQUILIBRIUM DATA IN REACTION 1, STATIC METHOD

Thermostat temp., °C.	Vapor press. of H_2O, mm. of Hg at 0°	Total equilib. press., mm. Hg at 0°	Time of run, hours	Furnace temp. °C.	K_1
50.94	96.4	119.5	4.0	773	0.240
50.94	96.4	119.5	2.0	771	.240
62.76	169.0	229.8	9.0	698	.359
62.75	169.0	233.0	14.0	658	.377
69.30	226.3	272.4	3.3	826	.203
69.30	226.3	270.0	2.0	826	.193
69.25	225.8	260.1	1.0	896	.152

As shown in Fig. 1, the results of the static and dynamic methods agree very closely at the lower temperatures, but show some tendency to diverge. At the highest temperature of the range common to both sets the deviation is some 9%. This amount is not greater than the estimated possible combined error of the measurements. We assume, therefore, that both sets are essentially correct.

To determine "best values" of K_1, Curve 3 of Fig. 1, which gives some weight to both series of results, has been drawn. From it the figures of Table IV have been taken. We are unable to ascribe any meaning to the figures published by Wöhler and Balz[5] and have omitted them from consideration.

TABLE IV

BEST VALUES OF EQUILIBRIUM CONSTANT OF REACTION 1

Temperature, °C.	650	700	750	800	850	900
$K_1 = (H_2)/(H_2O)$	0.456	0.340	0.266	0.213	0.174	0.144

Measurements in Reaction 2

The dynamic method described above is readily adaptable to the carbon system and was employed virtually unchanged in principle. In this case mixtures of carbon dioxide and carbon monoxide of known composition are passed through the reaction flask, the temperature of the furnace being raised or lowered to produce reduction or oxidation.

The same tin in the same flask and furnace with the same thermocouple were used in Reaction 2 as in Reaction 1. Gas mixtures of the desired composition were prepared by addition of carbon dioxide from calcium carbonate and hydrochloric acid to the mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with sulfuric acid. These gases were stored in aspirator bottles, using sodium bicarbonate solution as the confining liquid in order to reduce variations in the composition of the gas due to the changes in solubility of carbon dioxide caused by temperature and pressure changes. Before entering the reaction flask the gas stream was passed over calcium chloride. At the beginning and end of each run samples of gas from the aspirator were analyzed by absorption of carbon dioxide in sodium hydroxide and carbon monoxide in acid cuprous chloride solutions, the average of the closely agreeing results being taken as the equilibrium ratio corresponding to the temperature finally established in the furnace.

A typical series of observations with a ratio $(CO)/(CO_2) = 0.326$ is as follows.

E.m.f. of thermocouple, mv.	5.20	5 80	5.40	5.60	5 52	5.58	5.55
Condition of tin	ox.	red.	ox.	red.	ox.	red.	ox.

From these observations 5.56 mv., corresponding to 645°, was taken as the temperature of equilibrium of the solids with this gas mixture.

A summary of final results is contained in Table V and plotted in Fig. 2 (Curve 1).

TABLE V

EQUILIBRIUM CONSTANTS OF REACTION 2

Temperature, °C.	645	666	681	704	772	815
K_2 $(CO)/(CO_2)$	0.326	0.312	0.304	0.295	0.270	0.255

Our results are lower by some 20% than the figures for K_2 chosen by Maeda[3] from observations of gas compositions obtained on streaming carbon monoxide or carbon dioxide at low velocities over the solid phases at various temperatures. His smoothed results are shown in Curve 2 of Fig. 2. This method as applied by him does not approach in accuracy the one used by us. It may be said, however, that within the rather wide limits of error his work agrees with ours.

Comparison of our data with the average values obtained by Fraenkel and Snipischski[2] (Table 4a of their paper) is also made in Fig. 2. The curvature shown in the plot (Curve **3)** of their results is probably indicative of some error in their work. However, between 775 and 925° the mean slope of their curve is nearly the same as ours (extrapolated above 825°) and points from the two curves agree within 6%, well within the combined error. Below 775° the curves deviate, differing by 16% at 650°. It should also be mentioned that at about 950° a sharp change in slope shows in Fraenkel and Snipischski's curve. At the higher temperatures, not shown in the figure, their results either correspond to different solid phases or are seriously in error.

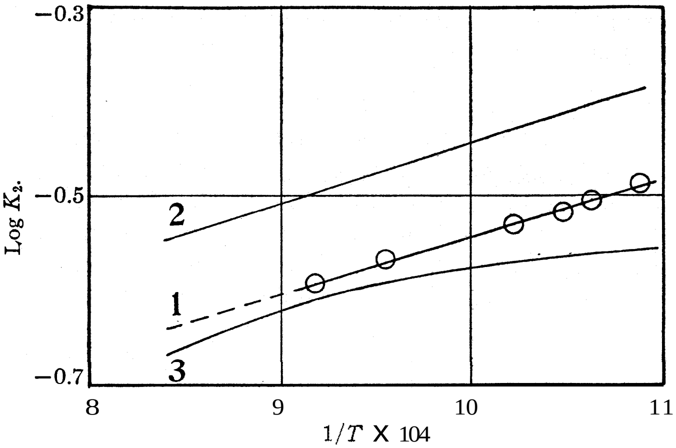

Fig. **2.—Equilibrium** constant of reaction 2. Curve 1, Eastman and Robinson; Curve 2, Maeda; Curve **3,** Fraenkel and Snipischski.

Our experiments permitted much greater precision than was attained either by Fraenkel and Snipischski or Maeda. We consider it justifiable to take points from Curve 1 of Fig. 2 as most representative of the equilibrium in this reaction. Table VI has been compiled in this way.

TABLE VI

BEST VALUES OF THE EQUILIBRIUM CONSTANT OF REACTION 2

Temperature, °C.	650	700	750	800	850	900
K_2 = (CO)/(CO_2)	0.321	0.296	0.277	0.260	0.245	0.232

The Water–Gas Equilibrium Constant

In calculating the water–gas constant the values of K_1 and K_2 determined under precisely similar conditions by our dynamic method will alone be utilized. These figures for K_2 have already been given in Table VI. Similar values for K_1, taken from Curve 1 of Fig. 1, are listed in the second column of Table VII. The calculated values of K_3 corresponding to these two sets are given in the third column of the table. Columns four, five and six, giving for comparison similar calculations from two equilibria in the iron system, and the directly determined values, are taken from the paper of Eastman and Evans.'

TABLE VII

VALUES OF THE EQUILIBRIUM CONSTANT OF THE WATER–GAS REACTION

Temp., °C.	K_1	K_3 from K_2/K_1	K_3 from FeO:Fe	Ka from FeO:Fe_3O_4	Ka direct measurement
650	0.455	0.707	...	..	...
700	.336	0.882	0.862	0.86	0.581
750	.257	1.078	1.062	1.04	.733
800	.201	1.294	1.280	1.24	.892

The new data support the previous conclusion that the directly determined values are in error.

Summary

Indirect determinations of the water–gas equilibrium constant have been made from studies of the reaction of water vapor and of carbon dioxide with tin at temperatures between 650 and 800". The results agree with previous indirect determinations and differ largely from the direct.

The data used in the calculation of the water-gas constant were obtained by a modification of the dynamic method of determination, in which the oxidizing or reducing effect of the gas stream is observed visibly. This method would appear to permit convenient and accurate measurements in other similar systems.

In confirmation of the method used, determinations by the static scheme due to Deville were made in the reaction of tin with water vapor. The latter measurements extend as high as 875°. They substantiate the results by the dynamic method.

Prom the various data considered, best values of the equilibrium constants of the two reactions above, at 50° intervals between 650 and 900°, have been tabulated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

AN IMPROVED GLASS MANOMETER

BY FARRINGTON DANIELS

RECEIVED FEBRUARY 8, 1928 PUBLISHED APRIL 5, 1928

There is a considerable demand for devices which permit pressure measurements of a system enclosed entirely by glass. They are valuable for use with corrosive materials or for experiments at high temperatures. Several typical ones are shown in Figs. 1 to 8.[1] In every case a measured air pressure is balanced through a sensitive diaphragm. The first and second use the principle of the optical lever, the third and fourth depend on the movement of a pointer, the fifth displaces a liquid in a capillary tube, the sixth makes a clicking sound when the wrinkled diaphragm moves, and the rest operate by closing an electrical circuit.

A new glass diaphragm developed in this Laboratory has proved to be so satisfactory that a brief description is offered. Its construction is shown in Figs. 9 to 12. A short platinum wire is sealed into a small glass rod about 1 cm. long and let down by a fine platinum wire to rest on the bottom of a thin glass bulb. The bulb is then flattened in a flame and the protruding mass of glass under the rod is melted flat with a small, hot flame. It is well to have one side of the diaphragm less flexible than the other, so that the rod is given a lateral motion. A second platinum wire is next sealed through the tube just above the bulb. It is broken off on the outside and covered over with melted glass. The fine platinum wire connected to the diaphragm contact is pushed down while the tube is being sealed into a flask or other container. It is then pulled out and attached to a heavier platinum wire which is sealed through the tube near the top. Another fine platinum wire provided with a loop is caught over the platinum contact at the side of the tube, pulled taut and sealed through the tube. The side contact is then adjusted with a stout wire to give a suitable zero reading, that is, to give electrical contact through a galvanometer and a high resistance when the pressure on the manometer side is slightly greater than the pressure in the flask. A radio grid leak or a beaker of distilled water serves as a convenient resistance. Asbestos wool is stuffed gently into the tube to keep the lead wires separated and to prevent cooling effects resulting from air circulation. The operation and calculations are similar to those described before.''

With ordinary glass the small rod attached to the diaphragm must be made of lead glass to avoid cracking of the diaphragm. With Pyrex glass the platinum wires are held firmly but the seals are not gas tight. This difficulty is removed by melting Pyrex glass over the end of the side contact and by covering the seals through which the lead wires pass with DeKhotinsky cement or lacquer.

Sections of tungsten wires may be used to advantage for sealing the lead wires through the Pyrex.

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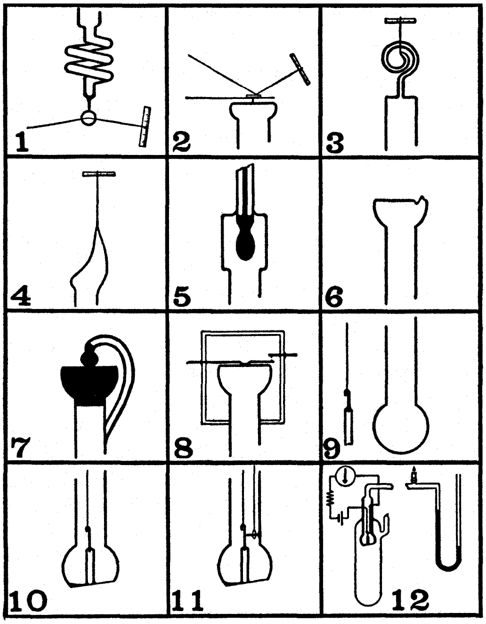
[1] (a) Ladenberg and Lehman, *Ber.*, **8**, 20 (1906); (b) Johnson, *Z. physik. Chem.*, **61**, 457 (1907); (c) Bodenstein and Katayama, *ibid.*, 69, 26 (1909); (d) Warburg and Leithauser, *Ann. Physik*, 24, 25 (1907); (e) Gibson, *Proc. Roy. Soc. Edinburgh*, **33**, 1 (1912); (f) Jackson, *J. Chem. Soc.*, 99, 1056 (1911); (g) Baume and Robert, *Compt. rend.*, **168**, 1199 (1919); (h) Smith and Taylor, THIS JOURNAL, 46, 1393 (1924); (i) Daniels and Bright, *ibid.*, 42, 1131 (1920); (j) Karrer, Johnston and Wulf, *J. Ind. Eng. Chem.*, **14**, 1015 (1922).

With quartz it is necessary to fuse the stout platinum wire contacts onto heavy tungsten wires in the oxygen flame and to anchor the tungsten wires in the quartz. A small capillary tube is fitted snugly over the tungsten wire and melted down with the oxygen flame. The quartz is then sealed in place. The lead wires are passed through holes and rendered gas tight with cement. For high temperatures the exit holes must be at a considerable distance from the furnace.

Several advantages of this diaphragm may be enumerated.

1. The construction and operation are relatively simple.



Devices for measuring gas pressures in all-glass vessels. Fig. 1.—Ladenberg and Lehman; Johnson. 2.—Warburg and Leithauser. 3.—Bodenstein and Katayama. 4.—Gibson; Jackson. 5—Baume and Robert. 6.—Smith and Taylor. 7.—Daniels and Bright. 8.—Karrer, Johnston and Wulf. 9–11.—Construction of improved diaphragm. 12.—Arrangement of finished apparatus.

2. The lever construction magnifies the motion and gives an excellent sensitivity.

3. The working parts are on the inside, instead of on the outside of the diaphragm, and a clumsy housing vessel for the diaphragm is not required.

4. The diaphragms always withstand a greater pressure outward than inward and the new construction makes it unnecessary to evacuate the manometer side before carrying out a measurement.

5. The whole of the diaphragm is well immersed in the chamber, giving isothermal conditions. Some of the other types are unsatisfactory for high temperatures because part of the diaphragm may be cooled by circulating air.

6. The contacts of platinum wire do not wear out and the zero point may be easily adjusted at any time. At temperatures below room temperature it is necessary to use a drying tube to prevent condensation of moisture on the contacts.

7. The zero point is independent of temperature over a wide range and it is independent of pressure until the total pressure becomes as low as 10 mm.

8. The apparatus may be made of ordinary glass, Pyrex or quartz. Pyrex glass is satisfactory up to 375°.

9. The chamber may be set up at a distance in a thermostat or other apparatus where direct observation is awkward.

One distinct disadvantage in comparison with the optical types lies in the fact that no warning is given when the zero is being approached. This difficulty is minimized by adjusting the manometer slowly through a capillary leak, or by placing a large bottle in the system as a pressure "buffer."

A full atmosphere's pressure on the manometer side does not break the diaphragm, even though the chamber is completely evacuated. The readings are usually accurate to 0.2 mm. of mercury. The sensitivity may be increased still further if the diaphragm is not required to withstand an atmosphere's difference in pressure. Occasionally the contacts become fouled, presumably by a speck of grease from the stopcock driven along by an inrush of air, but they may be readily regenerated by momentary sparking with a weak induction coil.

This type of manometer has been in constant use for three years in several different researches in this Laboratory and it has proved very satisfactory through many thousand pressure readings.

Summary

A device for measuring the pressure of a gas enclosed entirely in glass is described. A measured air pressure is balanced against the pressure of the enclosed gas through a glass diaphragm and the point of balance is obtained by closing an electrical circuit through a platinum contact fused to the diaphragm. Although similar to earlier devices the apparatus described here is more reliable and easier to construct.

MADISON, WISCONSIN

NOTES

Note on Electromagnetic Vacuum Cut-Off.—The accompanying diagram explains a type of mercury cut-off suitable for high vacuum work. The meniscus at B may be raised and lowered several millimeters by allowing the glass enclosed soft iron, D, in arm, A, to float on the mercury in this arm or be withdrawn entirely by means of a current passing through the magnet winding, which acts as a solenoid. The quantity of mercury is adjusted so that when the iron is withdrawn the top of the meniscus at B is just a millimeter or two below the opening of the inner tube. This permits an unimpeded flow of gas from the system to be evacuated to the pump. When the system is evacuated the iron is permitted to drop and the meniscus B then rises until the opening of the inner tube is effectively sealed off. It is more convenient to constrict very slightly the arm, A, at the top so that the iron weight will stick there when it is withdrawn by means of the solenoid. This permits the use of the cut-off either open or closed without a continuous flow of current. The weight will fall when the arm is lightly tapped with a pencil.

The size of the cut-off may be so designed that the whole apparatus can be immersed in liquid air and the mercury frozen in place, thus reducing the vapor pressure of the mercury. Otherwise a liquid air trap may be inserted between the cut off and the system to be evacuated. The former procedure is practicable only when the additional volume of such a trap is detrimental. Care must be taken to adjust the volume of arm **A** so that the meniscus B will not descend below C when atmospheric pressure is admitted to the system. The apparatus acts as a rough vacuum gage as well as a cut-off. It has the following advantages over the usual design of "Y" cut-off. The quantity of mercury is small and may be completely de-gassed. No fresh mercury is being constantly exposed. When atmospheric pressure suddenly enters the system the mercury level will drop so rapidly that no mercury is blown into the vacuum canalization. Contrary to a stopcock there is no chance for outside leakage and no vapor pressure from stopcock grease.

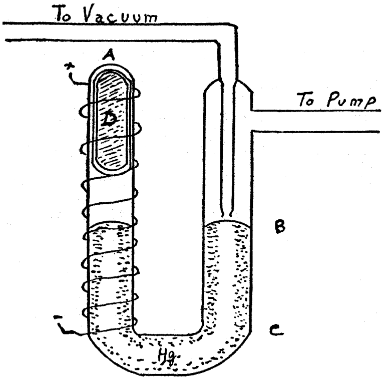


Fig. 1.—Electromagnetic vacuum cut-off.

CONTRIBUTION FROM THE
PHYSICAL CHEMISTRY LABORATORY
PRINCETON UNIVERSITY
JAMES H. HIBBEN

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Note in Reference to Platinum-Tungsten Welding.—Platinum may be welded direct to tungsten by the following method. The tungsten is cleaned with sodium nitrite. Several coats of platinum are burned into the tungsten from a solution of lavender oil and platinum chloride. The platinum to be welded is then coated with borax and welded to the tungsten in an oxygen flame. This must be done quickly. Gold may very easily be welded to tungsten by first cleaning the latter with the sodium nitrite, then covering with borax and finally plunging the heated tungsten into a molten gold bead. The gold makes an excellent flux for platinum welding when baser metals are a disadvantage.

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The Coefficient of Expansion of Bromoform.—Our attention was called by Professor Hildebrand to the fact that the only determination of the coefficient of expansion of bromoform to be found in the literature, that of Thorpe,[1] was evidently made with impure material, since its melting point was recorded as 2.5° instead of the more recent value[2] of 7.7°. We accordingly undertook a redetermination of this coefficient.

The bromoform used was purified by washing with sodium carbonate solution and then with water, drying for seventy-two hours over anhydrous calcium chloride and distilling three times under a pressure of about 20 mm. The melting points after each distillation were, respectively, 7.65, 7.70, 7.70°, as determined by a standardized thermometer graduated to 0.1°, which was immersed in the melting solid contained in a jacketed test-tube.

The coefficient of expansion was determined from the density at a series of temperatures ranging from 9 to 50°. A Pyrex pycnometer was used, having a volume of approximately 150 cc.

Beginning at 9°, and then at a series of successively higher temperatures, the pycnometer was immersed in a water-bath until temperature equilibrium was reached. The temperature of the bath was obtained

TABLE I

DATA AND RESULTS

Temp., °C.	Density. g./cc.	Specific volume	Molal volume
9.32	2.9187	0.34261	86.597
9.96	2.9178	.34273	86.626
13.93	2.9067	.34403	86.955
14.92	2.9048	.34426	87.014
15.00[a]	2.9043	.34431	87.027
18.73	2.8938	.34556	87.343
19.90	2.8918	.34581	87.404
20.00[a]	2.8912	.34588	87.423
23.21	2.8822	.34696	87.696
24.92	2.8787	.34737	87.801
25.00[a]	2.8780	.34746	87.823
27.92	2.8700	.34843	88.069
29.93	2.8656	.34897	88.203
32.43	2.8581	.34989	88.436
34.93	2.8525	.35057	88.608
38.65	2.8419	.35187	88.938
40.02	2.8393	.35219	89.019
42.71	2.8317	.35315	89.259
47.04	2.8201	.35459	89.625
50.27	2.8117	.35565	89.893

[a] These values were calculated from Equation (1).

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[1] Thorpe, *Proc. Roy. Soc. (London)*, **24**, 283 (1876).

[2] International Critical Tables, Vol. I.

by using a thermometer graduated to 0.1°, which was compared with one recently calibrated by the Bureau of Standards. The filled pycnometer was weighed at each temperature and the density, given in Table I, was calculated from these weights. The coefficient of cubical expansion of Pyrex glass used was that recently obtained by Buffington and Latimer.[3] All weights were reduced to vacuum.

No recent determination of the density of bromoform has been made and those in the literature are not in close agreement. However, that of Perkin,[4] 2.9045 g./cc. at 15°, and the value selected for the International Critical Tables, 2.890 at 20°, agree well with our values.

The following empirical equation for the variation of specific volume with temperature was obtained by the method of least squares from the data in Table I.

$$V_t = 0.24204\,[1 + 0.00090411\,(t - 7.7) + 0.0000006766\,(t - 7.7)^2] \qquad (1)$$

The values calculated by the aid of this equation differ by not more than three units in the last decimal place from the experimental points.

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The Freezing Point and Density of Pure Hydrogen Peroxide.—The above constants are of importance as criteria of the purity of peroxide. The freezing point as previously given[1] was taken when complete solidification took place, and the freezing bath was kept at a temperature several degrees below the freezing point of the peroxide. This gave too low a value, since the rate of crystallization of hydrogen peroxide is slow and the liquid has a great tendency to supercool. By a sufficient number of crystallizations a sample of peroxide was obtained which remained at a constant temperature during the whole process of solidification. The precaution necessary is to maintain the cooling bath at a temperature less than 0.1" below the freezing point, the liquid at the same time being continuously stirred. Under these conditions the melting point is −0.89°. The melting point −0.89° differs from that previously found by 0.90°, and this large difference must be ascribed to the slow rate of solidification which was not taken into account in the former work.

Special precautions were taken with regard to the dilatometer in the measurement of the density at 0° so that a minimum of decomposition occurred. Pyrex glass was found to be most suitable but only one out of a

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[3] Buffington and Latimer, THIS JOURNAL, 48, 2305 (1926).

[4] Perkin, J. *Chem. Soc.*, 45, 533 (1884).

[1] THIS JOURNAL, 42,2548 (1920).

large number of dilatometers could be used successfully, as too much decomposition was evident in the others. The value 1.4649 found for the density at 0° agrees within 1 part in 1500 with the previous[1] determinations 1.4633.

In a dilatometer slight decomposition often occurs as is evidenced by the formation of minute bubbles. The following method is then recommended. The dilatometer is connected as indicated in the diagram by means of a rubber tube "B" to one end of an open manometer having an adjustable mercury reservoir A. The reading of the meniscus of the dilatometer is taken at atmospheric pressure, p_1, and then the mercury is rapidly raised so that the enclosed gas in the dilatometer and connecting tubing is compressed to a pressure p_2 given by the manometer. The meniscus then gives a reading R_2 at the pressure p_2 as compared to the reading R_1 at the pressure p_1. The volume v of the oxygen produced in the decomposition of the peroxide is given by $v = K(R_1 - R_2) \div (1 - p_1/p_2)$, where K is the volume of the unit length of the capillary of the dilatometer. As an example, in an inferior dilatometer (5cc. capacity), three sets of meniscus readings were made at twenty-minute intervals and the volumes of the bubbles in the liquid estimated by the above method as 0.0086, 0.0156 and 0.0214 cc. With these corrections the densities calculated for each of the three sets of observations agreed within 1 part in 7000.

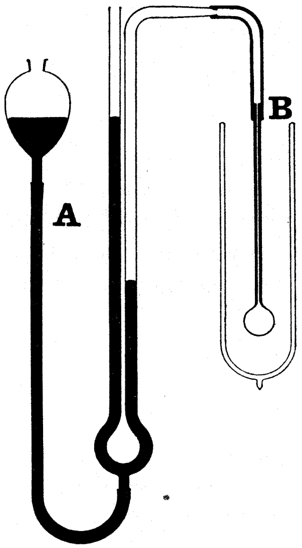

Fig. 1.

It was found that for concentrated aqueous solutions of peroxide containing up to 5% of water, the density could be accurately expressed by the equation D = 0.9486 + .005163 A, where A is the per cent. by weight of hydrogen peroxide.

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THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. III. THE INTERACTION OF MONATOMIC ALCOHOLS AND ESTERS WITH FUSED CAUSTIC ALKALIES[1]

BY H. SHIPLEY FRY AND EARL OTTO

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Introduction

Previous papers[2] have described the apparatus, experiments, and analytical methods employed, and the hypothesis proposed for the mechanism of the reactions occurring when the vapors of methyl alcohol, ethyl alcohol, formaldehyde, acetaldehyde and acetone were bubbled through an excess of fused, anhydrous equimolar mixtures of sodium and potassium hydroxides.

The quantitative investigations of these reactions showed that the carbon compounds undergo oxidation, usually to carbonates, with the liberation of hydrogen and frequently methane, in conformity with the general type reactions (M = Na or K)

$$R(H)_n + n\,MOH \longrightarrow R(OM)_n + n\,H_2$$
$$R(CH_3)_n + n\,MOH \longrightarrow R(OM)_n + n\,CH_4$$

These reactions apparently involve the acidic dissociation of the alkalies and the replacement of hydrogen or methyl radicals by OM radicals.

The present paper presents the results of an extension of the previously described procedure and principles to a further study of the reactions of (A) methyl and (B) ethyl alcohols and to an initial study of other monatomic alcohols—(C) normal propyl, (D) secondary propyl, (E) *iso*butyl and (F) tertiary butyl alcohols—and the simple esters, (G) methyl formate and (H) methyl acetate.

A. Methyl Alcohol

This further study of the behavior of methyl alcohol was suggested by a comment of one of the editors of THIS JOURNAL, to the effect that in order to make the argument more rigid, more attention should have been given to the intermediate steps involved in the proposed reaction mechanism scheme. These steps were assumed, in the case of methyl alcohol, to conform to the following scheme of consecutive reactions

$$CH_3OH + NaOH \longrightarrow CH_3ONa + H_2O \qquad (1)$$
$$CH_3ONa + HONa \longrightarrow CH_2(ONa)_2 + H_2 \qquad (2)$$

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[1] Synopsis of a section of a thesis presented to the Faculty of the Graduate School, University of Cincinnati, by Earl Otto, in partial fulfilment of the requirements for the degree of Doctor of Philosophy; also presented in part at the Philadelphia Meeting of the American Chemical Society, September, 1926.

[2] (a) Fry, Schulze and Weitkamp, THIS JOURNAL, 46, 2268 (1924); (b) Fry and Schulze, *ibid.*, 48,958 (1926); (c) Fry and Cameron, *ibid.*, 49,864 (1927).

$$CH_2(ONa)_2 + H_2O \longrightarrow CH_2O + 2HONa \tag{3}$$

$$\text{I, } \Sigma \text{ (1), (2), (3), } CH_3OH \longrightarrow CH_2O + H_2$$

$$CH_2(ONa)_2 + HONa \longrightarrow CH(ONa)_3 + H_2 \tag{4}$$

$$CH(ONa)_3 + H_2O \longrightarrow HCO_2Na + 2NaOH \tag{5}$$

$$\text{II, } \Sigma \text{ (1), (2), (4), (5), } CH_3OH + HONa \longrightarrow HCO_2Na + 2H_2$$

$$CH(ONa)_3 + HONa \longrightarrow C(ONa)_4 + H_2 \tag{6}$$

$$C(ONa)_4 + H_2O \longrightarrow Na_2CO_3 + 2NaOH \tag{7}$$

$$\text{III, } \Sigma \text{ (1), (2), (4), (6), (7), } CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$$

As evidence for this scheme, the summation reaction noted in Equation III and also the conversion of formaldehyde to carbonate with the liberation of hydrogen in conformity with the type equation, $CH_2O + 2NaOH \longrightarrow Na_2CO_3 + 2H_2$, have been quantitatively verified. Each of these reactions was effected at 300–325°, at which temperatures the intermediately formed methylate, formaldehyde and formic acid compounds of the alkali metals, indicated in partial Equations 1, 2 and 4, are quite unstable. They undoubtedly, as noted shortly, undergo immediate and practically complete oxidation at 300° to the final carbonate stage culminating in summation Equation III.

In order to secure further evidence for the occurrence of intermediate reactions, it was deemed advisable to conduct a series of eight independent runs, each in duplicate, with methyl alcohol, extending over a range of temperatures from 250 to 450°, and estimating quantitatively for each run the yields of hydrogen, carbonates and methyl alcohol present as methylates, and testing further the reaction residues for the presence of formaldehyde and formates predicted at lower temperatures.

In each run 10 cc. or 7.89 g. of absolute methyl alcohol was used. In place of the formerly employed equimolar mixture of the caustic alkalies, a eutectic mixture, melting point 185°, was used, namely, 51.1 g. of potassium hydroxide with 55.3 g. of sodium hydroxide. The yields of hydrogen and carbonates were determined as described in previous papers. The amounts of unaffected methyl alcohol present in the reaction residues as methylates of sodium and potassium were determined by alkaline permanganate titrations upon aliquot portions.

Formaldehyde was not found in any of the reaction residues. This was to be expected, since a separate run made at 250° with formaldehyde (obtained through depolymerization of trioxymethylene) showed practically complete oxidation to carbonate with only minute traces of intermediately formed alkali formates. In fact, the quantities of formates actually obtained (determined by the extent of their reducing action upon mercuric chloride), in the first four runs, namely at 250, 270, 290 and 310°, ranged from about 0.2 to 0.0%.

In Table I, following, the data for each temperature indicate the extent of the oxidation of methyl alcohol according to Equation III. Each figure is an average of two runs which checked within 5%.

TABLE I

THE EFFECT OF TEMPERATURE UPON THE INTERACTION OF METHYL ALCOHOL WITH FUSED CAUSTIC ALKALIES

Run	Temp., °C.	H_2 found, liters (0°/760 mm.)	H_2 calcd., % (eq. III)	CO_2 found, g.	CO_2 calcd., % (eq. III)	CH_3OH, g. recovered	CH_3OH, % recovered
1	250	0.9	5.6	0.73	6.7	7.19	91.1
2	270	2.6	16.0	2.02	18.8	5.65	71.6
3	290	7.6	46.1	5.24	48.6	2.09	26.6
4	310	12.8	76.9	7.68	71.2	.75	9.6
5	330	14.0	86.0	8.79	81.4	.19	2.4
6	350	14.4	86.9	8.92	82.6	.15	1.9
7	370	14.5	87.4	9.20	85.2	.09	1.3
8	450	16.6	99.9	10.69	98.8		

It is evident that as the temperature is increased, the extent of the oxidation of methyl alcohol, or the corresponding yields of hydrogen and carbonates, also increases in percentages commensurate with the stoichiometrical ratios required by summation Equation III.

The presence of methylates in the reaction residues from seven runs is evidence of the occurrence of reaction (1) noted in the reaction mechanism scheme. The presence of formates in the reaction residues from the first three runs, that is, at temperatures below 300°, indicates the occurrence of the intermediate reactions represented by equations (2), (4) and (5), summation of which with (1) gives Equation II. (Separate runs with formic acid showed its complete decomposition at 300° but accompanied with some carbonization.) Oxidation of methyl alcohol according to the final summation Equation III is 85% complete at 370° and 100% complete at 450°.

Incidentally,' a note should be incorporated relative to methyl alcohol runs made with sodium hydroxide and with potassium hydroxide separately. This was in compliance with a request from Professor J. R. Withrow, Chairman of the Committee of the National Research Council on Substitution of Sodium Compounds for the Conservation of Potassium Compounds, that we test the effect of the alkalies separately.

Three groups of runs, each in duplicate, were made with 10 cc. or 7.89 g. of methyl alcohol, the first with 117 g. of potassium hydroxide, the second with 83 g. of sodium hydroxide, and the third with a mixture of 51.1 g. of potassium hydroxide and 55.3 g. of sodium hydroxide, which has a lower melting point (185') than any other mixture. All runs were made at 450". The data are embodied in Table II.

The yields of hydrogen and carbonates with potassium hydroxide and sodium hydroxide, separately, are approximately 95% of the theoretical and nearly identical, but for the mixture of alkalies they are practically theoretical. These experiments also show that by working at sufficiently high temperatures sodium hydroxide could be substituted for potassium

TABLE II

EFFECT OF THE CAUSTIC ALKALIES SEPARATELY AND MIXED, RUN I (KOH), RUN II (NAOH), RUN III (KOH AND NAOH)

Run	H_2 found, liters (0°/760 mm.)	H_2 calcd., eq III	H_2, % of theory	CO_2 found, g.	CO_2 calcd., eq. III	CO_2, % of theory
Ia	16.1	16.6	96.7	9.32	10.82	86.0
Ib	15 6	16.6	93.7	10.23	10.82	94.4
IIa	16.0	16.6	96.2	10.56	10.82	97 4
IIb	15.9	16.6	95.2	9.82	10.82	91.6
IIIa	16.7	16.6	100.6	10.53	10.82	97.5
IIIb	16.5	16.6	99.4	10.85	10.82	100.2

hydroxide, but convenience in operation of this special method of conducting the reactions requires the use of a mixture, the fusion point of which is initially the lowest obtainable.

B. Ethyl Alcohol

When the type reaction mechanism is applied to ethyl alcohol, the following reactions are indicated

$$CH_3CH_2OH + NaOH \longrightarrow CH_3COONa + 2H_2 \qquad (8)$$

$$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4 \qquad (9)$$

$$\Sigma\ (8),\ (9) \quad CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4 \qquad (10)$$

In previous runs with ethyl alcohol at 250–280°, Fry and Schulze[2b] obtained not only hydrogen, methane, acetates and carbonates, the products of reactions (8) and (9), but also much ethylene, arising presumably according to equation (11).

$$CH_3CH_2OH \longrightarrow C_2H_4 + H_2O \qquad (11)$$

The incomplete interaction of ethyl alcohol at 250–280° and the simultaneous occurrence of reactions (8), (9) and (11) made it impossible in the earlier experiments to check the stoichiometrical ratios indicated and thereby establish the summation reaction, equation (10).

In these subsequent experiments, it has been found that runs made with 10 cc. (7.84 g.) portions of ethyl alcohol *at higher* temperatures gave lower yields of acetates, higher yields of carbonates, with hydrogen and methane approaching the relative volume ratio 2:1. In other words as the *temperature* is raised, *the* reaction tends to *conform* to the summation

TABLE III

ETHYL ALCOHOL DATA, 530°

	Run I	Run II		Run I	Run II
C_2H_5OH, g.	7.84	7.84	CH_4 calcd., liters (0°/760 mm.)	3.9	3.9
H_2 found, liters (0°/760 mm.)	7.8	8.2	CH_4 calcd., %	100	92
H_2 calcd., liters (0°/760 mm.)	7 9	7.9	Vol. ratio, H_2:CH_4	1.95:1	2.27:1
H_2 calcd., %	99	104	CO_2 found, g.	6.7	6.4
CH_4 found, liters (0°/760 mm.)	3.9	3.6	CO_2 calcd., g.	7.5	7.5
			CO_2 calcd., %	90	85

equation (10). This is clearly evident from the data of two duplicate runs (Table III) conducted at 530°. All calculations are based upon summation equation (10).

In this reinvestigation of the interaction of ethyl alcohol with fused caustic alkalies at higher temperatures, neither acetates nor ethylene were obtained; the quantitative data indicate practically complete oxidation of ethyl alcohol to carbonate with the liberation of hydrogen and methane in conformity with the proposed type reaction

$$CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4$$

C. Normal Propyl Alcohol

In view of this behavior of ethyl alcohol, it is natural to assume that normal propyl alcohol would react quite similarly to yield carbonates, hydrogen and ethane in conformity with the type equation (12)

$$CH_3CH_2CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + C_2H_6 \qquad (12)$$

Other equations, (13) and (14) following, indicating respectively more extensive and finally complete oxidation, may be derived by extending the type reaction to the other hydrogen atoms of the propyl alcohol molecule

$$CH_3CH_2CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + CH_4 + 5H_2 \qquad (13)$$

$$CH_3CH_2CH_2OH + 10NaOH \longrightarrow Na_2CO_3 + 2Na_4CO_4 + 9H_2 \qquad (14)$$

Equations (12), (13) and (14) represent three stages of oxidation of propyl alcohol by the fused caustic alkalies. To determine the actual extent of the oxidation, duplicate runs at 500° were made with 10 cc. or 8 g. portions of pure normal propyl alcohol according to the usual method. The alcohol reacted readily and completely, but the reaction residue, in addition to carbonates, was found to contain some free carbon. The gases evolved, collected and analyzed contained *no ethane* but *hydrogen* and *methane* in ratio by volume of about 4.3: 1.

The absence of methane precludes the reaction noted in equation (12); the presence of methane and the hydrogen-methane gas volume ratio indicate equation (13) and preclude equation (14). The presence of some free carbon in the reaction residue precludes the establishment of exact stoichiometrical ratios for any assumed reaction, but the data obtained approximate most closely those ratios indicated in equation (13). Ac-

TABLE IV

NORMAL PROPYL ALCOHOL DATA, 500°

	Run I	Run II		Run I	Run II
C_3H_7OH, g.	8.0	8.0	CH_4 calcd., liters (0°/760 mm.)	2.7	2.7
H_2 found, liters (0°/760 mm.)	11.9	10.4	CH_4 calcd., %	92.7	100.0
			Vol. ratio, H_2:CH_4	4.75:1	3.9:1
H_2 calcd., liters (0°/760 mm.)	14.6	14.6	CO_2 found, g.	8.79	8.26
H_2 calcd., %	81.5	73.8	CO_2 calcd., g.	11.7	11.7
CH_4 found, liters (0°/760 mm.)	2.5	2.7	CO_2 calcd., %	75.1	70.6

cordingly, for convenience of record and comparison, all of the **quantitative** data which follow in Table IV are based upon the stoichiometrical requirements of equation (13), which is apparently the dominant reaction occurring at 500°.

D. Isopropyl Alcohol

Since ethyl and normal propyl alcohols are oxidized by fused caustic alkalies to carbonates with the liberation of hydrogen and methane, it is naturally assumed that *iso*propyl alcohol will also react similarly according to the proposed type equation **(15)**

$$(CH_3)_2CHOH + 2NaOH \longrightarrow Na_2CO_3 + H_2 + 2CH_4 \qquad (15)$$

This assumption has been verified by the quantitative data obtained in duplicate runs at 500° with **20** cc. or 15.7 g. quantities of pure *iso*propyl alcohol. The sole products of the reactions were carbonates, hydrogen and methane, with very minute traces of free carbon in the reaction residue. The yields of the products, as recorded in Table V, are calculated in terms of the stoichiometrical ratios required by equation (15).

TABLE V

*Iso*PROPYL ALCOHOL DATA, 500°

	Run I	Run II
$(CH_3)_2CHOH$, g.	15.7	15.7
H_2 found, liters (0°/760 mm.)	11.5	11.3
H_2 calcd.. liters (0°/760 mm.)	11.5	11.5
H_2 calcd., %	100.0	98.3
CH_4 found, liters (0°/760 mm.)	5.7	5.5
CH_4 calcd , liters (0°/760 mm.)	5.8	5.8
CH_4 calcd., %	98.2	95.6
Vol. ratio, H_2:CH_4	1:2.04	1:2.05
CO_2 found, g.	10.94	10.84
CO_2 calcd., g.	11.40	11.40
CO_2 calcd., %	96.0	95.1

The above data confirm, within the limits of experimental error entailed in the method, the stoichiometrical ratios, $(CH_3)_2CHOH$: CO_2 : H_2 : $2CH_4$, required by the assumed type equation (15).

E. Isobutyl Alcohol

The three carbon chain compound, normal propyl alcohol, underwent some carbonization on interaction with the fused caustic alkalies, while ethyl and isopropyl alcohols, two carbon chain compounds, suffered little if any carbonization. It was accordingly expected that runs with isobutyl alcohol, a three carbon chain compound, would also be impaired by some carbonization. In fact, two runs with isobutyl alcohol, one at 350° and one at 500°, were accompanied by such extensive carbonization that results possessing any stoichiometrical significance could not be obtained.

F. Tertiary Butyl Alcohol

In view of the facts just noted, the isomer of isobutyl alcohol, namely the two carbon chain compound, tertiary butyl alcohol, should react with the fused caustic alkalies with little or no carbonization and yield carbonates and methane in conformity with the proposed type equation (16).

$$(CH_3)_3COH + 2NaOH \longrightarrow Na_2CO_3 + 3CH_4 \qquad (16)$$

To verify this equation, duplicate runs made at 500° with weighed samples of pure tertiary butyl alcohol gave reaction residues containing carbonates *free from carbon.* The gas evolved, as predicted, was chiefly methane but contained some hydrogen, undoubtedly a by-product of some minor secondary reaction, since the ratio by volume of methane to hydrogen was 24:1. Some of the tertiary butyl alcohol escaped interaction: it distilled unaffected through the fused alkalies, was condensed, recovered, weighed and deducted from the initial amount used. The yields of methane and carbonates, as recorded in Table VI, are calculated in terms of the stoichiometrical ratios required by equation (16).

TABLE VI

TERTIARY BUTYL ALCOHOL DATA, 500°

	Run I	Run II		Run I	Run II
$(CH_3)_3COH$, g.	14.4	11.8	CH_4 calcd., %	87.4	91.9
CH_4 found, liters (0°/760 mm.)	11.2	9.6	CO_2 found, g.	7.43	6.07
CH_4 calcd., liters (0°/760 mm.)	12.8	10.4	CO_2 calcd., g.	8.51	6.93
			CO_2 calcd., %	87.3	87.6

The yields of methane and carbonates are in conformity with the stoichiometrical ratio, $(CH_3)_2COH:3CH_4:CO_2$, required by the assumed type equation (16).

G. Methyl Formate

The interaction of methyl formate with the fused caustic alkalies may be assumed to involve three principal reactions. The first, equation (17), is the saponification of methyl formate yielding formate and methyl alcohol

$$HCOOCH_3 + NaOH \longrightarrow HCOONa + CH_3OH \qquad (17)$$

The second, equation (18), is the type reaction for the oxidation of formate to carbonate with liberation of hydrogen

$$HCOONa + NaOH \longrightarrow Na_2CO_3 + H_2 \qquad (18)$$

The third, equation (19), is the summation Equation III, previously developed and verified again in Section A, indicating complete oxidation of methyl alcohol to carbonate with evolution of hydrogen

$$CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2 \qquad (19)$$

The summation of equations (17), (18) and (19) gives equation (20) which is the assumed reaction for the complete oxidation of methyl formate

$$HCOOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 4H_2 \qquad (20)$$

To test the validity of this assumption (that is, equation 20), several runs were made with pure methyl formate, which, on account of its low boiling point (32°) could not be introduced into the tube bearing the fused alkalies in the customary manner directly from a Walther dropping funnel. The methyl formate (about 10 cc.) was first introduced into a weighed gas liquefying bulb with inlet and outlet stopcocks. The outlet stopcock was connected by glass tubing to the apparatus containing the fused alkalies. Opening of the exit cock and gentle warming of the gas liquefying bulb permitted a steady flow of methyl formate vapor through the caustic alkalies, which were maintained at 475°. Reweighing of the tube after vaporization of its contents gave the weight of methyl formate used.

Reaction took place readily in each of the three runs. The gas evolved was pure hydrogen. The reaction residue contained the carbonates *with some* free carbon. (When separate runs were made *with* formic acid, free carbon was *likewise* formed.) The quantitative data are noted in Table VII. The calculations are based upon the previously developed summation equation (20).

TABLE VII

METHYL FORMATE DATA, 475°

Run	HCO_2CH_3 g.	H_2 found, liters (0°/760 mm.)	H_2 calcd., liters (0°/760 mm.)	H_2 calcd., %	CO_2 found, g.	CO_2 calcd., g.	CO_2 calcd., %
I	6.57	8.0	9.8	81.5	8.1	9.6	71.1
II	8.62	11.1	12.9	86.2	10.1	12.6	70.6
III	8.23	10.1	12.3	82.3	9.7	12.1	70.0

In these runs with methyl formate, the yields of hydrogen, based on equation (20), are ten or more per cent. greater than the corresponding yields of carbonate. Nevertheless, the data show that at least 70% of the methyl formate was oxidized to carbonate with the liberation of hydrogen in conformity with the assumed type reaction equation (20).

H. Methyl Acetate

The extended application of the type reactions to methyl acetate leads directly to equations which are exactly parallel to those proposed for methyl formate. In other words, the following equations (21), (22), (23) and (24) are, respectively, similar to the previously proposed equations, (17), (18), (19) and (20).

$$CH_3COOCH_3 + NaOH \longrightarrow CH_3COONa + CH_3OH \qquad (21)$$

$$CH_3COONa + NaOH \longrightarrow Na_2CO_3 + CH_4 \qquad (22)$$

$$CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2 \qquad (23)$$

$$(21), (22), (23)\ CH_3COOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + CH_4 + 3H_2 \qquad (24)$$

The extent to which this summation equation (24) has been verified is shown by the quantitative data of duplicate runs with 9.28 g. samples of pure methyl acetate made at 475° and recorded in Table VIII. The reaction residues contained carbonates but no free carbon. The gases evolved were hydrogen and methane.

TABLE VIII

METHYL ACETATE DATA, 450°

	Run I	Run II		Run I	Run II
CH_3COOCH_3, g.	9.28	9.28	CH_4 calcd., liters (0°/760 mm.)	2.79	2.79
H_2 found, liters (0°/760 mm.)	9.01	9.02	CH_4 calcd., %	92.2	99.6
H_2 calcd., liters (0°/760 mm.)	8.44	8.44	Vol. ratio, $H_2:CH_4$	3.37:1	3.24:1
H_2 calcd., %	106.7	106.8	CO_2 found, g.	9.57	9.79
CH_4 found, liters (0°/760 mm.)	2.58	2.78	CO_2 calcd., g.	11.03	11.03
			CO_2 calcd., %	86.8	88.7

While the checks for the yields of the several products of the reaction are in fair agreement, there are certain deviations from the stoichiometrical ratios ($CH_3COOCH_3:3H_2:CH_4:2CO_2$) required by the summation equation (24) which call for further comment.

The excessive yields of hydrogen over methane and carbonates indicate some further oxidation of the methyl radical or methane not accounted for in equation (24). The yield of carbonates is nearly 88% of the theoretical. This indicates that, notwithstanding the excessive yields of hydrogen, about 88% of the methyl acetate was oxidized to carbonate in conformity with the proposed summation equation (24).

Other investigations, runs similar to those described, were made with the following compounds: ammonia, monomethyl-, dimethyl- and trimethyl- amines and dimethyl and diethyl ether. In each case, there was no evidence obtained indicating the occurrence of any chemical change whatsoever. In other words, the vapors of the compounds noted resisted the oxidizing action of the fused caustic alkalies.

It is again a pleasure to express our appreciation of the continued interest of Dr. Ernst Twitchell, the donor of the graduate fellowship stipends which have made the continuation of the work described in this and the two following papers possible.

Summary

The special method, apparatus and hypothesis suggested for the mechanism of the reactions, investigated quantitatively as described in previous papers,[2] have been extended to a further investigation of the behavior of methyl and ethyl alcohols, and to initial studies of the behavior of normal propyl, *iso*propyl, *iso*butyl and tertiary butyl alcohols, and to the simple esters, methyl formate and methyl acetate.

With methyl alcohol further evidence has been adduced through duplicate series of runs extending over a wide range of temperatures, 250450°, confirming certain intermediate reactions assumed to occur according to the proposed type equation

$$RH_n + n\,MOH \longrightarrow R(OM)_n + n\,H_2 \quad (M = Na \text{ or } K)$$

In the investigations of the behavior of other monatomic alcohols and simple esters at temperatures between 450 and 550°, data have been obtained which, within the limits of experimental error necessarily entailed in the methods employed, substantiate the occurrence of the reactions predicted in conformity with the following equations originally developed by applying the type reactions, RH, $+$ n MOH $\longrightarrow$ R-(OM), $+$ n H_2, and $R(CH_3)_n$ $+$ n MOH $\longrightarrow$ $R(OM)_n$ $+$ n CH_1), to the molecules of the compounds investigated. In every instance oxidation of the carbon compound by the fused caustic alkalies yielded carbonates, hydrogen and methane, thus

Methyl alcohol $CH_3OH + 2NaOH \longrightarrow Na_2CO_3 + 3H_2$
Ethyl alcohol $CH_3CH_2OH + 2NaOH \longrightarrow Na_2CO_3 + 2H_2 + CH_4$
Normal propyl alcohol $CH_3CH_2CH_2OH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 5H_2 + CH_4$
Isopropyl alcohol $(CH_3)_2CHOH + 2NaOH \longrightarrow Na_2CO_3 + H_2 + 2CH_4$
Isobutyl alcohol (Extensive carbonization precluded determination of any stoichiometric ratios)
Tertiary butyl alcohol $(CH_3)_3COH + 2NaOH \longrightarrow Na_2CO_3 + 3CH_4$
Methyl formate $HCOOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 4H_2$
Methyl acetate $CH_3COOCH_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 3H_2 + CH_4$

The following compounds resisted the action of the fused caustic alkalies: NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $(CH_3)_2O$, $(C_2H_5)_2O$.

Further investigations are described in the following articles, Parts IV and V of the series.

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. IV. THE INTERACTION OF GLYCOL AND GLYCEROL WITH FUSED CAUSTIC ALKALIES[1]

BY H. SHIPLEY FRY AND ELSE L. SCHULZE

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The principles and procedure described in the preceding papers of this series[2] are here extended to a quantitative study of the interactions of the polyatomic alcohols, glycol and glycerol, with the fused eutectic mixture of sodium and potassium hydroxides.

Glycol

In 1859, Wurtz[3] found that on heating a mixture of glycol (5 g.) and potassium hydroxide (8 g.) to 250°, hydrogen (4325 cc. at 19°/768 mm.)

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[1] Summary of a section of the doctorate research of Else L. Schulze. Presented at the Philadelphia Meeting of the American Chemical Society, September, 1926.

[3] (a) Fry, Schulze and Weitkamp, THIS JOURNAL, 46, 2268 (1924); (b) Fry and Schulze, *ibid.*, 48, 958 (1926); (c) Fry and Otto, *ibid.*, 50, 1122 (1928).

[3] Wurtz, Ann. *chim.* phys., [3] 55, 417 (1859).

was evolved. The reaction residue consisted of potassium oxalate with small amounts of carbonate and glycolate. The quantities were not recorded. Wurtz proposed an equation for the reaction which, translated into modern formulas, becomes

$$C_2H_6O_2 + 2KOH \longrightarrow K_2C_2O_4 + 4H_2$$

The yield of hydrogen, based upon the limited quantity of alkali used, is 63% of the theoretical.

Another quantitatively significant record of the action of caustic alkalies upon glycol is that of Nef,[4] who heated equimolar quantities of ethylene glycol (60 g.) and pulverized sodium hydroxide (38.7 g.) for two and one-half hours at 230–284°. He thus obtained 25 liters of hydrogen and various products: di- and tri-ethylene glycol (17.4 g.); glycolic acid (14 g. as the calcium salt); small amounts of methyl and ethyl alcohols; and formic, acetic, oxalic and carbonic acids as sodium salts. The yields obtained do not establish stoichiometrical ratios for any particular reaction. This may be due to Nef's not having used an excess of alkali and to the manner of effecting the interaction, which did not permit the possibility of homogeneous mixing and interaction afforded by the present method.

When Nef treated ethylene glycol with an excess of potash lime at 250°, hydrogen was liberated and carbonates only were formed, but no record of the yields was noted.

An application of the proposed type reaction mechanism (that is, the type equation $R(H)_n + n\ MOH \longrightarrow R(OM)_n + n\ H_2$) to the hydrogen atoms of the glycol molecule not only serves to account for the intermediate products but also results in the development of summation equations for more complete oxidation reactions which may be verified by establishing the stoichiometrical ratios indicated therein. The scheme of partial and summation equations, involving the application of the type reaction to the hydrogen atoms united to both carbon atoms of glycol, is as follows

$$CH_2OHCH_2OH + 2NaOH \longrightarrow CH_2ONaCH_2ONa + 2H_2O \qquad (1)$$

$$CH_2ONaCH_2ONa + 4NaOH \longrightarrow C(ONa)_3C(ONa)_3 + 4H_2 \qquad (2)$$

$$C(ONa)_3C(ONa)_3 + 2H_2O \longrightarrow CO_2NaCO_2Na + 4NaOH \qquad (3)$$

$$\Sigma\ (1), (2), (3)\ CH_2OHCH_2OH + 2NaOH \longrightarrow CO_2NaCO_2Na + 4H_2 \qquad (4)$$

$$CO_2NaCO_2Na + NaOH \longrightarrow HCO_2Na + Na_2CO_3 \qquad (5)$$

$$HCO_2Na + NaOH \longrightarrow Na_2CO_3 + H_2 \qquad (6)$$

$$\Sigma\ (4), (5), (6)\ CH_2OHCH_2OH + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \qquad (7)$$

It is quite significant that equation (4), the summation of partial equations (1), (2) and (3), is identical with the reaction proposed by Wurtz. Equation (5) indicates further oxidation of the oxalate to formate and to carbonate, the products noted by Nef, while equation (7), the summation

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[4] Nef, *Ann.*, 335, 310 (1904).

of (4), (5) and (6), that is, all of the intermediate steps, represents complete oxidation of glycol to carbonate and hydrogen.

An explanation of the formation of glycolic acid, also found by Nef in the reaction residue, readily follows through the application of the type reaction mechanism when limited to the hydrogen atoms of but one of the two carbon atoms of glycol, thus

$$CH_2OHCH_2OH + NaOH \longrightarrow CH_2OHCH_2ONa + H_2O \tag{8}$$

$$CH_2OHCH_2ONa + 2NaOH \longrightarrow CH_2OHC(ONa)_3 + 2H_2 \tag{9}$$

$$CH_2OHC(ONa)_3 + H_2O \longrightarrow CH_2OHCO_2Na + 2NaOH \tag{10}$$

$$\Sigma\ (8),\ (9),\ (10)\quad CH_2OHCH_2OH + NaOH \longrightarrow CH_2OHCO_2Na + 2H_2 \tag{11}$$

The summation of equations (8), (9) and (10) gives equation (11), which accounts for the formation of glycolic acid.

The further extension of the type reaction mechanism to the hydrogen atoms of the other carbon atom of glycolic acid gives equation (12) which, with equation (11), gives the summation equation (13) identical with summation equation (7) representing, as previously noted, complete oxidation of glycol to carbonate.

$$CH_2OHCO_2Na + 3NaOH \longrightarrow 2Na_2CO_3 + 3H_2 \tag{12}$$

$$(11),\ (12)\quad CH_2OHCH_2OH + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \tag{13}$$

Thus the proposed reaction mechanism scheme not only explains the formation of all the intermediate and final reaction products noted by Wurtz and Nef, but also suggests the following experiments, the purpose of which is to determine how nearly the stoichiometrical ratios, $(CH_2OH)_2:CO_2:5H_2$, of summation equation (7) or (13) for complete oxidation of glycol, may be verified.

To this end runs in triplicate were conducted, one at 250° and two at 350°, with 10 cc. (11.15 g.) quantities of glycol, supplied through the courtesy of the Globe Soap Company, and purified to correct b. p. 197.5°. In each of the runs four hours was occupied in adding the glycol from the Walther dropping funnel to the fused caustic alkalies.

In the run at 250°, the evolution of hydrogen, with minute traces of methane ceased after a twenty hour heating period. No distillate was obtained. The reaction residue consisted almost entirely of the hydroxides and carbonates of sodium and potassium with small quantities of oxalates, equivalent to about 0.5 g. of oxalic acid.

In the runs at 350°, the evolution of hydrogen with traces of methane ceased after five to seven hours' heating. A distillate too minute for investigation had a characteristic aromatic odor. The reaction residue consisted entirely of the hydroxides and carbonates of sodium and potassium *with no trace of oxalates,* indicative of the complete oxidation reaction noted in equation (7) or (13).

The experimental data are summarized in Table I. All calculations are based upon summation equation (7) or (13).

TABLE I

GLYCOL DATA: RUN I (250°); RUNS 11 AND III (350°)

Run	$C_2H_4(OH)_2$, g.	H_2 found. liters°	H_2 calcd liters[a]	H_2 calcd., %	CO_2 found, g.	CO_2 calcd., g.	CO_2 calcd., %
I	11.15	15.75	20.15	78.17	13.00	15.83	82.13
II	11.15	15.92	20.15	79.01	13.66	15.83	86.30
III	11.15	15.63	20.15	77.57	13.21	15.83	83.45

[a] At 0° and 760 mm.

The data show that the reaction for the complete oxidation of glycol at 250° and at 350° to carbonates, with the liberation of hydrogen, has been effected to the extent of practically 80% of the theoretical yields required by the proposed summation equation (7) or (13).

Glycerol

The interaction of glycerol with various alkalies has been widely investigated. A survey of the work of a number of investigators[5,4] reveals many different experimental procedures covering wide ranges of temperatures with heterogeneous reaction mixtures, and consequently a great variety of oxidation products. The few quantitative data recorded do not establish stoichiometrical relationships for any particular reactions occurring. The products obtained, the results *of* partial or incomplete *oxidations* of glycerol by the alkalies, are as follows: hydrogen and methane; methyl, ethyl, propyl, *iso*propyl, allyl alcohols and propylene glycol; salts of formic, acetic, lactic, acrylic, propionic, butyric, oxalic and carbonic acids.

It is the purpose of the present investigation, which employs a slow and regulated addition of glycerol, with temperature control, to a homogeneous reaction mixture of fused caustic alkalies: (1) to determine the possibility of verifying predictions suggested by the application of the type reaction mechanism to all of the hydrogen atoms of the glycerol molecule, thereby effecting complete oxidation of glycerol to carbonates, and (2) to consider the bearing of the quantitative data obtained upon the apparently contradictory observations of Buisine and of Nef.

The application of the type reaction mechanism to the glycerol molecule, resulting in a summation equation which indicates ultimate oxidation of glycerol to carbonates with the liberation of hydrogen, is as follows.

$$CH_2OHCHOHCH_2OH + 3NaOH \longrightarrow CH_2ONaCHONaCH_2ONa + 3H_2O \quad (1)$$

$$CH_2ONaCHONaCH_2ONa + 5NaOH \longrightarrow C(ONa)_3C(ONa)_2C(ONa)_3 + 5H_2 \quad (2)$$

$$C(ONa)_3C(ONa)_2C(ONa)_3 + 4NaOH \longrightarrow 3C(ONa)_4 + 2H_2 \quad (3)$$

$$3C(ONa)_4 + 3H_2O \longrightarrow 3Na_2CO_3 + 6NaOH \quad (4)$$

$$(1), (2, (3, (4) \quad CH_2OHCHOHCH_2OH + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \quad (5)$$

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[5] (a) Redtenbacher, Ann., 47, 137 (1843); (b) Herter, *Ber.*, 11, 1167 (1878); (c) Belohoubek, *Ber.*, 12, 1872 (1879); (d) *Bull. soc. chim.*, [2] 34, 160 (1880); (e) Fernbach, *ibid.*, [2] 34, 146 (1880); (f) Raisonnier, *ibid.*, [3] 7, 534 (1892); (g) Buisine, *Compt. rend.*, 136, 1082, 1204 (1903).

The extent to which the summation equation (5) may be verified will be considered after reviewing briefly the pertinent work of Buisine and of Nef.

Buisine[5a] studied the reactions of glycerol at various temperatures with *an excess of potassium hydroxide mixed with potash lime* in order to establish a method for the quantitative determination of small amounts of glycerol calculated upon the volume of hydrogen liberated. The temperatures and the equations for the corresponding reactions postulated by Buisine are as follows:

$$\begin{array}{llr}
220\text{–}250^\circ & C_3H_8O_3 + 2KOH \longrightarrow CH_3CO_2K + HCO_2K + H_2O + 2H_2 & (6)\\
250\text{–}280^\circ & 2C_3H_8O_3 + 4KOH \longrightarrow 2CH_3CO_2K + K_2C_2O_4 + 2H_2O + 5H_2 & (7)\\
280\text{–}320^\circ & 2C_3H_8O_3 + 6KOH \longrightarrow 2CH_3CO_2K + 2K_2CO_3 + 2H_2O + 6H_2 & (8)\\
320\text{–}350^\circ & C_3H_8O_3 + 4KOH \longrightarrow 2K_2CO_3 + CH_4 + H_2O + 3H_2 & (9)
\end{array}$$

Buisine recommended the employment of equations (8) and (9) at 320 and 350°, respectively, as best adapted to give yields of hydrogen for calculating quantities of glycerol, but he recorded no quantitative data other than the volumes of gases evolved to verify the other stoichiometrical requirements for the yields of the other intermediate oxidation products, namely, the formates, acetates, oxalates and carbonates of potassium. Nevertheless, it is quite significant that equations (6), (7), (8) and (9) represent successive and further degrees of oxidation of glycerol occurring as the temperature increases. The ultimate oxidation to carbonate only (see Equation 5 in preceding reaction mechanism scheme) was not considered by Buisine. It should also be noted that each of Buisine's equations may be derived, *a priori*, by an application of the type reaction mechanism to a selected number of the hydrogen atoms of the glycerol molecule, but when all are involved, presumably at higher temperature, the reaction represented by equation (5) occurs, as will be shown later.

Nef heated 309 g. of glycerol and 137 g. of pulverized sodium hydroxide at 270–280° from six to eight hours and obtained methyl, propyl and allyl alcohols, lactic and propionic acids and salts of oxalic and carbonic acids. No record was noted of the quantity of hydrogen liberated in this experiment. *The quantity of alkali used by Nef was considerably less than that required for the completion of any of the reactions postulated by Buisine.* In another experiment Nef heated, at 270–325° for three hours, 20 g. of glycerol with 60 g. of potash lime, *not an excess as* employed by Buisine but comparable to the quantity required by the Buisine equation (8), and obtained predominantly the salts of propionic and carbonic acids with traces of formates, oxalates and acetates, and twelve liters of hydrogen. Buisine, *at the same temperature (280–320°), but with an excess of potash lime, obtained only acetates and carbonates and a practically theoretical yield of hydrogen (Equation 8).* The corresponding yield of hydrogen obtained by Nef without an excess of potash lime was about 40% of the theoretical.

These marked differences in the results of Buisine and Nef find an explanation in the fact that Buisine employed an excess of alkali while Nef did not. Furthermore, the number of intermediate reaction products, indicative of limited oxidation of glycerol, is decreased as the temperature is increased. At sufficiently high temperature oxidation primarily to carbonates is effected. These conclusions are further substantiated by the quantitative data obtained in the following runs with glycerol.

Three runs were conducted, each with approximately 10 cc. of previously crystallized glycerol (b. p. 290°), supplied through the courtesy of the Globe Soap Company, and added at the rate of two drops per minute to the excess of the fused caustic alkalies. The temperature was maintained at 345–360° for eight hours, at the end of which time gas evolution had almost ceased. The temperature was then raised to and maintained at 400° for three hours, thereby effecting the evolution of more gas, which finally ceased after heating at 450° for another three hours. About two-thirds of the total volume of gases evolved was collected at 350°. *The apparent cessation of the reactions at 350° indicated completion of the intermediate oxidation reactions noted in the Buisine equations (6), (7), (8) and (9), while further heating at 400° and at 450° promoted the reaction of the previously developed equation (5) representing oxidation solely to carbonate.*

Since it has been found in the three runs made that *the reaction residue contained only carbonates* and that *the gases evolved were hydrogen and methane in the volume ratio of about* $5H_2:CH_4$, the conclusion is apparent that two *reactions* were ultimately concurrent, namely, that of the Buisine equation (9) yielding hydrogen, methane and carbonates in the stoichiometrical ratio $3H_2:CH_4:2CO_2$ and that of equation (5) yielding hydrogen and carbonates in the stoichiometrical ratio $7H_2:3CO_2$.

In order to facilitate record and subsequent reference, the complete oxidation equation *(5)* will now be designated as reaction **(A)** and the Buisine equation (9) for partial oxidation as reaction (B), thus

$$C_3H_5(OH)_3 + 6NaOH \longrightarrow 7H_2 + 3Na_2CO_3 \qquad (A)$$

$$C_3H_5(OH)_3 + 4NaOH \longrightarrow 3H_2 + CH_4 + 2Na_2CO_3 + H_2O \qquad (B)$$

and the quantitative data of the three runs may be employed to calculate approximately the extent to which reactions (A) and (B) occurred.

If a and b represent the respective volumes of hydrogen liberated, and x and y the respective yields of carbonates (as CO_2) in the reactions (A) and (B), then $a:x = 7H_2:3CO_2$ and $b:y = 3H_2:2CO_2$. Having determined $(a + b)$ and $(x + y)$, the quantities of glycerol respectively oxidized by the caustic alkalies according to reactions **(A)** and (B) may be calculated. The analytical data and results of these calculations are summarized in Table II.

The analytical data and calculations indicate that within the limits of experimental error necessarily involved in the methods of procedure, an average of 18.72% of the initial quantity of glycerol employed was completely oxidized to carbonate according to reaction (A), while an average of 67.92% was partially oxidized to carbonate according to re-

TABLE II

GLYCEROL DATA

Run	H = (a + b), liters[a]	$CO_2 = (x + y)$, g.	(a) liters[a] calcd.	(b) liters[a] calcd.	(x), g., calcd.	(y), g., calcd.
I	9.35	10.2	4.37	4.98	3.68	6.35
II	9.83	11.22	3.54	6.30	2.98	8.25
III	9.21	10.58	3.18	6.04	2.68	7.91
Average	9.46	10.67	3.70	5.77	3.11	7.50

Run	$C_3H_5(OH)_3$, g. used	$C_3H_5(OH)_3$, g. ⇔ x eq. (A)	$C_3H_5(OH)_3$, g. ⇔ y eq. (B)	$C_3H_5(OH)_3$, % reacting, eq. (A)	$C_3H_5(OH)_3$, % reacting, eq. (B)
I	11.4	2.57	6.82	22.55	59.85
II	12.3	2.08	8.62	16.92	70.09
III	11.2	1.87	8.27	16.70	73.84
Average	11.6	2.17	7.90	18.72	67.92

[a] At 0° and 760 mm.

action (B). Thus 86.64% average of all of the glycerol used may be accounted for in terms of reactions (A) and (B), the former dominating at about 450°, while the latter, according to Buisine, is the dominant reaction at 350°. If the quantity of glycerol escaping interaction (about 14% of the initial quantity used amounting to 1.6 g., which represents the amount very likely adhering to the walls of the apparatus) be disregarded, then of the glycerol entering into reaction 21% was oxidized according to reaction (A) and 78% according to reaction (B).

Summary

The application of the type reaction mechanism to the glycol and glycerol molecules leads to the development of equations for reactions accounting for the intermediate and final products obtained by previous investigators.

The apparently contradictory results of Buisine and of Nef have been explained by showing that the various oxidation products obtained are dependent upon the quantities of alkalies used, the temperatures employed, time of heating and the homogeneity of the reaction mixtures. As the temperature is increased, fused alkalies being present in large excess, further oxidation occurs and fewer intermediate products are obtained; at sufficiently high temperatures complete oxidation to carbonates with the liberation of hydrogen is effected.

Under the special method of investigating the oxidizing action of the fused sodium and potassium hydroxides upon glycol and glycerol, which permits their slow addition to a homogeneous reaction mixture *with* constant *temperature* control, quantitative data have been obtained which indicate the occurrence of the following reactions: complete oxidation of glycol at 350° to carbonates with liberation of hydrogen (Equation 5); partial oxidation of glycerol at 350° to carbonates with the liberation of hydrogen and methane (Reaction B), while complete oxidation to carbonates with

the liberation of hydrogen (Reaction A) is promoted by raising the temperature to 450°. At 450° about 20% of the glycerol was oxidized according to reaction (A) and 78% according to reaction (B).

The proposed equations for these reactions, derived through an application of the type reaction mechanism and quantitatively verified within the limits of experimental error necessarily entailed in the method of procedure, are as follows

$$C_2H_4(OH)_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 5H_2 \qquad (5)$$
$$C_3H_5(OH)_3 + 6NaOH \longrightarrow 3Na_2CO_3 + 7H_2 \qquad (A)$$
$$C_3H_5(OH)_3 + 4NaOH \longrightarrow 2Na_2CO_3 + 3H_2 + CH_4 + H_2O \qquad (B)$$

CINCINNATI, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

THE LIBERATION OF HYDROGEN FROM CARBON COMPOUNDS. V. THE INTERACTION OF DEXTROSE, LEWLOSE, SUCROSE AND CELLULOSE WITH FUSED CAUSTIC ALKALIES[1]

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Introduction

The results obtained in a quantitative study of the interaction of a number of monatomic alcohols[2] and the polyatomic alcohols, glycol and glycerol,[3] with a eutectic mixture of fused sodium and potassium hydroxides naturally leads to an extension of the previously described principles and procedure[4] to several polyhydroxy compounds—dextrose, levulose, sucrose and cellulose.

The type reaction mechanism applied to sugars and cellulose leads to equations accounting for a great variety of intermediately formed oxidation products; but since, in this study, the carbon compounds have been either (1) completely oxidized to carbonate with the liberation of hydrogen or (2) partially oxidized to carbonate with the liberation of methane and hydrogen, only these two types of reactions will be considered.

Dextrose and Levulose

The literature records no quantitatively verified equations for such specific reactions of dextrose and levulose with the caustic alkalies under

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[1] Synopsis of a section of a thesis presented by Earl Otto to the Faculty of the Graduate School, University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. Read before the Lexington Section, February 9, 1927, and the Cincinnati Section, February 23, 1927, of the American Chemical Society.

[2] Fry and Otto, THIS JOURNAL, 50, 1122 (1928).

[3] Fry and Schulze, *ibid.*, 50,1131 (1928).

[4] (a) Fry, Schulze and Weitkamp, *ibid.*. 46, 2268 (1924); (b) Fry and Schulze, *ibid.*, 48,958 (1926); see also (c) Fry and Cameron, *ibid.*, 49,864 (1927).

present methods of procedure. Two lines of approach for the development of the corresponding type equations, herewith proposed for verification, may be considered: (1) the fact that dextrose and levulose are known to yield lactates, and (2) the reaction whereby dextrose and levulose give ethyl alcohol and carbon dioxide.

Omitting intermediate type equations, the two following abbreviated schemes may be considered as applicable to dextrose and levulose.

SCHEME I

$$C_6H_{12}O_6 = 2C_3H_6O_3 = 2CH_3CH(OH)CO_2H \qquad (1)$$

$$2CH_3CH(OH)CO_2H + 2NaOH \longrightarrow 2CH_3CH(OH)CO_2Na + 2H_2O \qquad (2)$$

$$2CH_3CH(OH)CO_2Na + 6NaOH \longrightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 \qquad (3)$$

$$\Sigma\ (1),\ (2),\ (3)\quad C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 + 2H_2O \qquad (A)$$

Equation (1) notes the assumed empirical equivalency of one molecule of dextrose or levulose to two molecules of lactic acid; equation (2), the formation of sodium lactate; equation (3), the oxidation of sodium lactate. Summation equation (A) indicates oxidation of dextrose or levulose to carbonate with liberation of methane and hydrogen. The other approach to a summation equation is through the assumed formation of ethyl alcohol and carbon dioxide.

SCHEME II

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2 \qquad (4)$$

$$2C_2H_5OH + 4NaOH \longrightarrow 2Na_2CO_3 + 2CH_4 + 4H_2 \qquad (5)$$

$$2CO_2 + 4NaOH \longrightarrow 2Na_2CO_3 + 2H_2O \qquad (6)$$

$$\Sigma\ (4),\ (5),\ (6)\quad C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2 \qquad (A)$$

Equation (4) notes the equivalency of dextrose or levulose to ethyl alcohol and carbon dioxide; equation (5), quantitatively verified in previous investigations with ethyl alcohol, shows oxidation to carbonate with liberation of methane and hydrogen; equation (6) notes conversion of carbon dioxide to carbonate. The summation of equations (4), (5) and (6) again gives equation (A), identical with the summation equation of Scheme I. Thus in either scheme equation (A) indicates oxidation to carbonate with liberation of methane and hydrogen in the stoichiometrical ratio $2CO_2:CH_4:2H_2$.

Oxidation of all of the carbon of dextrose or levulose to carbonate with the liberation of hydrogen only is indicated thus

$$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2 \qquad (B)$$

In equation (B) the stoichiometrical ratio is $CO_2:2H_2$, that is, twice the volume of hydrogen called for in equation (A).

In all runs made with dextrose and levulose, *carbonates, methane* and *hydrogen* were the products of the reactions. *The volume of hydrogen evolved was greater than that indicated in equation (A) but less than that noted in* equation *(B)*. These facts clearly indicate the concurrence of reactions **(A) and** (B). An exactly similar situation has been shown to exist in the previously described runs with glycerol. The approximate extent to which reactions (A) and (B) occur have been ascertained as follows.

Since sugars could not be introduced in the vapor or liquid state to the fused caustic alkalies, as was done with previously investigated compounds, duplicate mixtures of weighed and pulverized samples of the purest available dextrose and levulose (Kahlbaum) with the pulverized caustic alkalies were introduced into the iron tube of the apparatus. In order to avoid carbonization and effect uniformity in the reaction mixtures, they were heated to fusion temperature, 185°, and then to 300–310" for at least an hour. The temperature was then gradually raised through a period of fourteen hours' heating to 550°. The evolution of gases was marked at 375° and ceased at 550°. The alkali residue showed very little carbonization. The reaction residue and gases were analyzed in the usual way.

If a and b represent the respective volumes of hydrogen liberated, and x and y the respective yields of carbonates (here recorded as volumes of CO_2) in the reactions (A) and (B),

$$C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2 \qquad (A)$$

$$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2 \qquad (B)$$

then $a:x = H_2:CO_2$ and $b:y = 2H_2:CO_2$. Having determined $(a + b)$ and $(x + y)$, the quantities of dextrose or levulose respectively oxidized by the caustic alkalies according to reactions (A) and (B) may be calculated. The analytical data and results of these calculations are summarized in the following Tables, I and II, for dextrose and levulose, respectively.

TABLE I

DEXTROSE DATA

	Run I	Run II		Run I	Run II
$H_2 = (a + b)$, liters"	8 33	8.46	Dextrose used, g.	16 21	16.25
$CO_2 = (x + y)$, liters[a]	7 44	7 22	Dextrose, g. ≎ x, eq. (A)	14.48	13.22
(a), liters," calcd.	6 55	5 98	Dextrose, g. ≎ y, eq. (B)	1 04	1 83
(b), liters," calcd.	1 78	2.48	Dextrose, % reacting, eq. (A)	89 4	81.4
(x), liters," calcd.	6 56	5 98	Dextrose, % reading, eq. (B)	6 4	11 2
(y), liters," calcd.	.89	1 24	Dextrose, % total reacting	95 8	92 6

[a] At 0° and 760 mm.

TABLE II

LEVULOSE DATA

	Run I	Run II		Run I	Run II
$H_2 = (a + b)$, liters[a]	7.05	7.46	Levulose used, g	14 85	14 30
$CO_2 = (x + y)$, liters"	6 84	6 68	Levulose, g. ≎ x, eq. (A)	13.32	11.85
(a), liters,' calcd.	6 63	5 90	Levulose, g. ≎ y, eq. (B)	.82	1.05
(b), liters,' calcd.	.42	1.56	Levulose, % reacting, eq. (A)	90 0	82 9
(x), liters," calcd.	6.63	5 90	Levulose, % reacting, eq. (B)	1.8	7.3
(y), liters," calcd.	.21	.78	Levulose, % total reacting	91.8	90 2

[a] At 0° and 760 mm.

In summary, 90–95% of both dextrose and levulose taken underwent oxidation. Of the quantities of dextrose and levulose interacting, an average of the data shows that 90 or more per cent. of each was converted to carbonate with the liberation of methane and hydrogen (Equation A), while the balance was oxidized to carbonate with the liberation of hydrogen only (Equation B).

Sucrose

Since sucrose is a condensation product of dextrose and levulose, it would naturally be assumed, from the preceding observations and data, that it would be'oxidized by the fused caustic alkalies to yield carbonate, methane and hydrogen in quantitative ratios commensurate with the summation of the yields obtained from dextrose and levulose. This assumption could not be verified.

Repeated runs conducted with sucrose gave the expected products qualitatively, but in each run extensive carbonization, excessive frothing of the reaction mixture and constant clogging of the apparatus with charred matter precluded all attempts to determine the quantitative yields of the products and thereby establish any stoichiometrical ratios for the proposed reactions.

Cellulose

In 1829 Gay-Lussac[5] discovered that oxalates could be prepared from carbohydrates by fusion with alkalies. Erdmann[6] later noted that by altering conditions, primarily temperature, acetates were formed through the oxidation of carbohydrates. Hoppe-Seyler[7] treated cellulose (Swedish filter paper) with water and sodium hydroxide at temperatures up to 250°. Below 200° only mercerization took place, but with concentrated solutions at 220–240°, 360 cc. of *gas,* chiefly hydrogen with traces of methane, per gram of cellulose was evolved. Salts of formic, acetic and other fatty acids with oxalic, protocatechuic acid and protocatechol were obtained. Carbonates also were detected but not determined quantitatively. Fischer and Schrader,[8] performing similar experiments, obtained identical products and, in addition, salts of lactic acid. Heuser, Winsvold, and Herrmann[9] have effected a 90% conversion of cellulose at 270–280° with fused caustic potash to potassium oxalate.

Very recently, Sven Odén and S. Lindberg[10] made an exhaustive study of the interaction of cellulose with concentrated solutions of sodium hydroxide in an autoclave at 372° under 241 atmospheres' pressure and

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[5] Gay-Lussac, *Ann. chim. phys.,* [2] 41,398 (1829).

[6] Erdmann, *Ann. Suppl.,* 5,228 (1867).

[7] Hoppe-Seyler, *Z. physiol. Chem.* **13,** 77 (1889).

[8] Fischer and Schrader, *Ges. Abhandl. Kenntnis Kohle, 5,* 332 (1920).

[9] Heuser, Winsvold, and Herrmann, *Cellulosechemie,* 4, 49, 62 (1923).

[10] Odén and Lindberg, *Ind.* Eng. *Chem., 19,* 132 (1927).

obtained a variety of products including hydrogen, traces of methane and carbonates. They came to the conclusion that "the first stage of the decomposition is the splitting up of the cellulose into glucose which is known to yield lactic acid on treatment with alkali."

The application of the type reaction mechanism to cellulose will explain the formation (compare similar case with glycerol) of the intermediate products noted by earlier investigators. The products obtained, as previously explained, depend primarily upon the temperature of the reaction and the concentration of the alkalies. While Odén and Lindberg state that "no single formula *will* account for the *results* obtained," it may logically be assumed that a formulation of equations for reactions yielding carbonates, methane and hydrogen may be made provided that the reaction is conducted according to the present method of procedure.

The type reaction mechanism scheme applied to cellulose leads to two summation equations indicating partial oxidation to carbonate with liberation of methane and hydrogen (Equation A) and complete oxidation to carbonate and orthocarbonate with liberation of hydrogen only (Equation B).

$$C_6H_{10}O_5 + 8NaOH \longrightarrow 4Na_2CO_3 + 2CH_4 + 4H_2 + H_2O \qquad (A)$$

$$C_6H_{10}O_5 + 14NaOH \longrightarrow 5Na_2CO_3 + Na_4CO_4 + 12H_2 \qquad (B)$$

In the first runs conducted to establish the extent to which reactions (A) and (B) might take place, the purest cellulose obtainable, that is, Swedish filter paper previously digested with hydrochloric and hydrofluoric acids, was dried, cut into small squares and intimately mixed with the pulverized anhydrous alkalies. On heating the mixture, hydrogen, methane and carbonates were obtained but with extensive carbonization which precluded satisfactory establishment of the required stoichiometrical ratios.

In order to avoid carbonization and effect more intimate mixing, other runs were made wherein weighed quantities of cellulose were mixed to a thick paste with water and the alkalies. On gradually raising the temperature of these reaction mixtures, no gas was evolved until 250° was reached. All of the water distilled over between 200 and 400°. The evolution of gas ceased at 550°. The total time of heating occupied eight hours. Carbonization was not evident. The data of duplicate runs are noted in Table III, to which is appended an average of the two runs figured on the basis of a 10g. sample of cellulose.

TABLE III

CELLULOSE DATA

Run	Cellulose, g.	H_2 found, liters[m]	CH_4 found, liters[a]	CO_2 found, liters[m]	Ratio by vol., H_2:CH_4
I	8.17	10.56	0.23	5.45	43 : 1
II	9.47	12.21	.49	6.10	26 : 1
Av.	10.0	12.89	.46	6.55	33 : 1

[a] At 0° and 760 mm.

The excessive yields of hydrogen over methane indicate that the dominant reaction is in conformity with equation (B) rather than equation (A). The extent of the occurrence of both reactions, (A) and (B), may be estimated, as usual, on the basis of the average data for the: 10g. sample of cellulose noted in Table III. Let (a) and (b) represent the respective volumes of hydrogen liberated, and (x) and (y) the respective yields of carbonates, calculated as volumes of CO_2, in the reactions (A) and (B). Thus, $a:x = H_2:CO_2$, and $b:y = 2H_2:CO_2$. $(a + b)$ and $(x + y)$ are known. The calculations are summarized in Table IV.

TABLE IV

CELLULOSE DATA FOR CONCURRENT REACTIONS (A) AND (R)

Cellulose used, g.	10	(y), calcd., liters[a]	6.34
$H_2 = (a + b)$ liters"	12.89	Cellulose, g. ≎ x, eq. (A)	.38
$CO_2 = (x + y)$ liters"	6.55	Cellulose, g. ≎ y, eq. (B)	7.64
(a), calcd., liters[a]	.21	Cellulose, % reacting, eq. (A)	76.40
(b), calcd., liters[a]	12.68	Cellulose, % reacting, eq. (B)	3.80
(x), calcd., liters[a]	.21	Cellulose, % total reacting	80.20

[a] At 0° and 760 mm.

The average data indicate that 3.8% of the cellulose used reacted according to equation (A) while 76.4% reacted according to equation (B). In more direct figures, 5% of the cellulose reacting was partially oxidized to carbonate with the liberation of methane and hydrogen, while 95% was completely oxidized to carbonate with the liberation of hydrogen only. These results not only check the excessive yield of hydrogen over methane, noted by Odén and Lindberg,[10] but further confirm, at least to the extent of 80% of the theoretical yields, the possibility of indicating equations for the specific oxidation reactions which take place under the conditions of the special method of procedure herewith employed.

By way of comparison, it is also of interest to note that in the two types of reactions, (A) and (B), which indicate different extents of oxidation, the monoses, dextrose and levulose, react almost entirely in conformity with the limited oxidation type reaction (A), while under practically the same conditions cellulose is oxidized almost entirely in conformity with the complete oxidation type reaction (B).

Again it is a pleasure to express our gratitude for the interest and encouragement given by Dr. Ernst Twitchell in the progress of this work through his awards of fellowship stipends.

Summary

The application of the type reaction mechanism to dextrose, levulose and cellulose leads to the formulation of equations for reactions which, under the special method of procedure, have been quantitatively verified within the limits of experimental error.

Both dextrose and levulose, 90 to 95% of the quantities used, were oxidized to carbonates with the liberation of methane and hydrogen. Ninety per cent. or more of the quantities reacting is oxidized in conformity with the equation,

$$C_6H_{12}O_6 + 8NaOH \longrightarrow 4Na_2CO_3 + 2H_2O + 2CH_4 + 4H_2$$

while the balance reacts according to the equation

$$C_6H_{12}O_6 + 12NaOH \longrightarrow 6Na_2CO_3 + 12H_2$$

Under identical conditions sucrose underwent carbonization to such an extent that the possibility of verifying any proposed equations for reactions occurring was precluded.

Cellulose was completely oxidized, about 95% of the quantity reacting, in conformity with the equation

$$C_6H_{10}O_5 + 14NaOH \longrightarrow 5Na_2CO_3 + Na_4CO_4 + 12H_2$$

while the remaining 5% reacted according to the equation

$$C_6H_{10}O_5 + 8NaOH \longrightarrow 4Na_2CO_3 + H_2O + 2CH_4 + 4H_2$$

CINCINNATI, OHIO

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

RESEARCHES ON ACRIDINES. IV. THE PREPARATION OF HYDROXY-ACRIDINES AND DIFFERENT 5-POSITION ACRIDINE DERIVATIVES

BY H. JENSEN AND F. RETHWISCH[1]

RECEIVED SEPTEMBER 23, 1927 PUBLISHED APRIL 5, 1928

Introduction

In a previous paper a new method for the preparation of acridine derivatives has been outlined.[2] It has been shown that the treatment of o-aminobenzaldehyde with the halogen derivatives of nitrobenzene and with the corresponding derivatives of toluene would yield the corresponding diphenylamine derivatives. These diphenylamine derivatives split off water very easily to form acridine compounds. The authors have examined the general application of this reaction and have found that it can be extended in two ways. Halogen compounds of benzene, other than those mentioned, can be used, or the aminobenzaldehyde can be replaced by o-aminophenylketones.

The halogen derivatives of phenols were chosen first for the following reason. K. Matsumura[3] has described the preparation of 1(9)-hydroxyacridine by reduction of the corresponding acridone compound in boiling

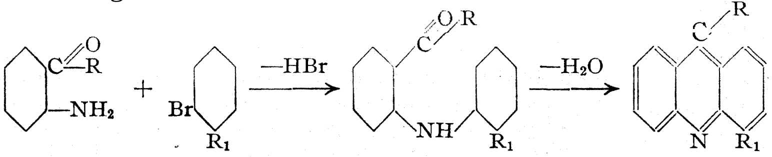
[1] A part of this paper is an abstract of a thesis presented by F. Rethwisch in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of Louisville.

[2] Jensen and Friedrich, THIS JOURNAL, 49, 1049 (1927).

[3] Matsumura, *ibid.*, 49, 816 (1927).

amyl alcohol with sodium. These results seemed open to question because it was believed that the dihydro-acridine derivative should be obtained, since acridine itself will give dihydro-acridine under the stated conditions. As our products are identical with those of the Japanese chemist, no hydrogenation of the acridine ring occurred during the reduction. In this work the free phenols could not be used as the hydroxy group itself reacted. For this reason the methyl and ethyl ethers were used.

Next the o-aminobenzaldehyde was replaced by o-aminophenylketones. This reaction should lead to 5-position acridine derivatives according to the following scheme



For R the investigations included the methyl and phenyl groups, and for R_1 the methyl, nitro and alkoxy groups, which were in either ortho or para position to the halogen. In all cases it was possible to secure the corresponding acridine compounds without great difficulty.

F. Mayer[4] has shown that the chlorine in o-chloro-acetophenone is not labile enough to react with aromatic amino compounds to give the corresponding diphenylamine derivatives, as is the case with *o*-chlorobenzophenone. It was thought that by introducing a nitro group in the para position to the halogen, the latter could be made more reactive. It was found that the chlorine in 5-nitro-2-chloro-acetophenone reacts very readily with aniline to give the corresponding diphenylamine derivative. The latter could be converted very easily into 3(7)-nitro-5-methylacridine, which has also been prepared in a different way. Experiments indicate that the chlorine in 5-nitro-2-chloro-acetophenone reacts also with o- and *p*-nitro-aniline. These products would give dinitromethylacridines in the final step of the reactions. It would be interesting to see if the chlorine in 5-nitro-2-chlorobenzaldehyde would react similarly.

The preparation of the methyl and ethyl esters of the acridine-5-carboxylic acid may also be reported. It is intended to use these esters as the starting materials for the preparation of different acridine compounds. The acridine-5-carboxylic acid could not be esterified with alcohol and hydrochloric acid, either by letting the mixture stand in the cold for several days or by heating for two days. No reaction could be obtained with sulfuric acid and alcohol. Pfitzinger[5] observed the same phenomenon in the cases of β-methyl- and of β-phenyl-cinchonic acids, as did also

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[4] F. Mayer and H. Freund, Ber., 55, 2054 (1922).

[5] Pfitzinger, *J. prakt. Chem.*, [2] 33, 100 (1886); 38, 582 (1888); 56, 283 (1897).

Borsche[6] in the case of the tetrahydro-acridine-5-carboxylic acid. Steric hindrance will probably account for this behavior of the acridine-5-carboxylic acid. The esters can be obtained from the acid chloride, which can be prepared by heating the acid with thionyl chloride.

The melting points given in this work are all uncorrected. They were, however, made with the same thermometer under identical conditions.

Experimental

The following acridine derivatives were prepared (Table I).

The following general procedure was adopted for preparing these acridine derivatives. Six g. of *o*-aminobenzaldehyde—in the case of the 5-methylacridine *o*-amino-acetophenone was used—a slight excess of the theoretical amount of the corresponding halogen derivatives of benzene, 0.4 g. of copper powder, 10 g. of anhydrous sodium carbonate and 60 cc. of nitrobenzene were refluxed for three hours at 220°. The nitrobenzene and the excess of the halogen derivatives of benzene were removed by steam distillation. The residue was extracted with ether, the ether solution dried over sodium sulfate, filtered and then evaporated. The condensation product was dissolved in 15 cc. of glacial acetic acid, and 3 cc. of concd. sulfuric acid was added.[7] This mixture was then heated on a water-bath for five minutes, poured into ice water and filtered. The filtrate was made alkaline with ammonium hydroxide. The precipitate was crystallized from the solvent given in the table.

The hydrolysis of the alkoxy-acridine to the corresponding hydroxy-acridine was effected by boiling the substance for one hour with hydriodic acid (sp. gr. 1.7) and traces of red phosphorus. The solution was then diluted with water and made alkaline with sodium hydroxide. The filtrate was made neutral with acetic acid. The precipitate was crystallized from the given solvent.

The derivatives of 5-methyl- and 5-phenylacridine were prepared in a similar way, except that o-amino-acetophenone or *o*-aminobenzophenone[8] was used instead of the *o*-aminobenzaldehyde.

As the melting point of our 5,3(7)-dimethylacridine was not in agreement with that given by Bonna,[13] we repeated his experiment.

Pure acetyl-*p*-tolylamine was used in this synthesis. The melting point of the product obtained from this was also 90°. The mixed melting point showed no depression. The same was true with the picrate. The product of Bonna might be the 5,2(8)-dimethyl compound.[9] This has the m. p. 122–123° which is given by Bonna for his product.

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.91; H, 6.32. Found: C, 87.12; H, 6.60.

Picrate: Anal. Calcd. for $C_{15}H_{13}N.C_6H_3O_7N_3$: C, 57.79; H, 3.70. Found: C, 57.89; H, 4 07.

Condensation Product of *o*-Aminobenzaldehyde and *o*-Bromo-anisole.[10]—The gen-

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[6] Borsche, *Ann.*, 377, 70–123 (1910).

[7] It was found in many cases that glacial acetic acid with a few cc. of concd. sulfuric acid was more satisfactory in closing the ring than was concd. sulfuric acid alone. If only sulfuric acid was used, sulfonation sometimes took place, and in the case of the ethoxy compound partial hydrolysis of the ether group was effected.

[8] Ullmann and Bleier, Ber.. 35, 4273 (1902).

[9] Borsche, Ann., 377, 97 (1902).

[10] The intermediate diphenylamine derivatives in these reactions are hard to isolate because at the high temperature used some ring closure takes place. For this reason we did not spend much time in trying to isolate them.

TABLE I

MONO SUBSTITUTION PRODUCTS OF ACRIDINE

Substance	Formula	M. p., °C.	Solvent	Crystal form	Color	% Carbon Calcd.	% Carbon Found	% Hydrogen Calcd.	% Hydrogen Found
3(7)-Ethoxy-acridine	$C_{15}H_{13}ON$	99	Dil. alc.	Plates	Yellow	80.68	80.51	5.87	6.12
Picrate of 3(7)-ethoxy-acridine	$C_{15}H_{13}ON.C_6H_3O_7N_3$	Did not melt at 250	Acetone	Needles	Yellow	55.74	55.97	3.57	3.81
Hydrochloride of 3(7)-ethoxy-acridine	$C_{15}H_{13}ON.HCl$	Decomposed at 200	Alcohol	Needles	Bright yellow	Calcd. Cl, Found Cl,		13.65 13.71	
3(7)-Hydroxy-acridine	$C_{13}H_9ON$	Did not melt at 250	Alcohol	Needles	Yellow	79.97	79.85	4.65	5.02
1(9)-Methoxy-acridine	$C_{14}H_{11}ON$	130–131	75% alc.	Needles	Light yellow	80.35	80.28	5.30	5.44
Picrate of 1(9)-methoxy-acridine	$C_{14}H_{11}ON.C_6H_3O_7N_3$	Decomposed at 250	Alcohol	Needles	Orange-red	54.79	54.63	3.22	3.18
1(9)-Hydroxy-acridine[3]	$C_{13}H_9ON$	116.5	75% alc.	Needles	Yellow	79.97	80.00	4.65	4.77
Picrate of 1(9)-hydroxy-acridine[3]	$C_{13}H_9ON.C_6H_3O_7N_3$	216	Alcohol	Needles	Red	53.77	53.62	2.85	3.14
5-Methylacridine	$C_{14}H_{11}N$	114	Petroleum ether	Needles	Slightly yellow	87.01	87.13	5.74	5.92
Picrate of 5-methyl-acridine	$C_{14}H_{11}N.C_6H_3O_7N_3$	213–214	Alcohol	Needles	Yellow	56.86	57.21	3.34	3.61

TABLE II

DI-SUBSTITUTION PRODUCTS OF ACRIDINE

Substance	Formula	M. p., °C.	Solvent	Crystal form	Color	% Carbon		% Hydrogen	
						Calcd.	Found	Calcd.	Found
5,3(7)-Dimethylacridine	$C_{15}H_{13}N$	90	Petroleum ether	Plates	Cream	86.91	86.84	6.32	6.52
Picrate of 5,3(7)-dimethylacridine	$C_{15}H_{13}N . C_6H_3O_7N_3$	Darkened at 215 Melted at 225	Alcohol	Needles	Yellow	57.79	57.96	3.70	3.92
3(7)-Nitro-5-methylacridine	$C_{14}H_{10}O_2N_2$	Did not melt at 300	Alcohol	Needles	Brown-yellow	70.57	70.63	4.23	4.42
1(9)-Nitro-5-phenylacridine[11]	$C_{19}H_{12}O_2N_2$	189–190	Alcohol	Needles	Yellow	75.98	75.92	4.03	4.21
3(7)-Nitro-5-phenylacridine[12]	$C_{19}H_{12}O_2N_2$	209–210	Alcohol	Needles	Yellow	75.98	76.07	4.03	4.18
3(7)-Methyl-5-phenylacridine[13]	$C_{20}H_{15}N$	135	Alcohol	Needles	Brown	89.18	89.27	5.62	5.87
Picrate of 3(7)-methylacridine	$C_{20}H_{15}N . C_6H_3O_7N_3$	226	Alcohol	Needles	Yellow	...	...	..	..
3(7)-Ethoxy-5-phenylacridine	$C_{21}H_{17}ON$	105–107	Alcohol	Plates	Yellow	84.25	84.18	5.73	5.96
3(7)-Hydroxy-5-phenylacridine[14]	$C_{19}H_{13}ON$	Darkened at 260 Sintered without melting at 275	Dil. alc.	Leaves	Yellow	84.10	84.23	4.83	5.03

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[11] F. Mayer, ref. 4, gives the melting point of this product as 218°. Time was not available for repeating his experiment.

[12] Ullmann, *Ber.*, **39,** 301 (1906).

[13] Bonna, *Ann.*, **239,** 63 (1887).

[14] Hess and Bernthsen, *Ber.*, **18,** 695 (1885); Kehrmann and Stépanoff, *Ber.*, **41,** 4138 (1908).

eral procedure was followed. The residue left after steam distillation was purified, giving light yellow needles from petroleum ether, m. p. 99°.

Anal. Calcd. for $C_{14}H_{13}O_2N$: C, 73.96; H, 5.77. Found: C, 73.91; H, 6.04.

Preparation of **2-Acetyl-4'-nitrodiphenylamine.**—It was prepared from *o*-aminoacetophenone and p-nitrobromobenzene. The residue left after steam distillation was crystallized several times from alcohol; yellow needles, m. p. 152°.

Anal. Calod. for $C_{14}H_{12}O_3N_2$: C, 65 60; H, 4.72. Found: C, 65.51; H, 5.03.

Condensation of 5-Nitro-2-chloro-acetophenone with Aniline.—Four g. of nitrochloro-acetophenone,[15] 4 g. of potassium carbonate and 5 cc. of freshly distilled aniline were heated for three hours at 170–180° and the mixture extracted with hot alcohol. The crystals from this were crystallized from alcohol as light yellow needles, m. p. 125°.

Anal. Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.60; H, 4.72. Pound: C, 65.68; H, 5.07.

The condensations of 5-nitro-2-chloro-acetophenone with o- and p-nitro-aniline were carried out in a similar way.

3(7)-Nitro-5-methylacridine.—Ring closure of the preceding 2-acetyl-4-nitrodiphenylamine was again obtained with acetic acid and sulfuric acid. The properties were the same as for the product prepared from 2-acetyl-4'-nitrodiphenylamine.

Anal. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.57; H, 4.23. Found: C, 70.48; H, 4.53.

Ethyl Ester of Acridiie-5-carboxylic Acid.—Six and five-tenths g. of acridine-5-carboxylic acid[16] and 20 g. of thionyl chloride were refluxed for two hours in a flask which was connected to a reflux condenser by a ground glass joint. The excess of thionyl chloride was removed by extracting three times with absolute benzene. Then the residue was filtered and washed several times with benzene. The acid chloride was immediately refluxed with 50 cc. of absolute ethyl alcohol. After all the chloride had gone into solution, water was added and the solution was made alkaline with sodium carbonate. The precipitate was purified from ligroin. The ethyl ester precipitates out in yellow, rhombohedral plates, m. p. 78°.

Anal. Calcd. for $C_{16}H_{13}O_2N$: C, 76.47; H, 5.22. Found: C, 76.53; H, 5.18.

Picrate.—Flaky yellow needles from alcohol, m. p. 226°.

Anal. Calcd. for $C_{16}H_{13}O_2N.C_6H_3O_7N_3$: C, 54.99; H, 3.36. Found: C, 55.23; H, 3.62.

Hydrochloride.—Yellow needles which did not melt at 250°

Anal. Calcd. for $C_{16}H_{14}O_2NCl$: Cl, 12.33. Found: Cl, 12.25.

Methyl Ester of Acridine-5-carboxylic Acid.—Crystallized from methyl alcohol in slightly yellow needles, m. p. 126.5–127.5°.

Anal. Calcd. for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.68. Found: C, 76.12; H, 4.55.

Picrate.—Yellow needles, m. p. 229–230°.

Anal. Calcd. for $C_{15}H_{11}O_2N.C_6H_3O_7N_3$: C, 54.07; H, 3.03. Found: C, 54.35; H, 3.41.

Hydrochloride.—The yellow needles did not melt at 250°.

Anal. Calcd. for $C_{15}H_{12}O_2NCl$: Cl, 12.96. Found: Cl, 12.88.

Summary

The method described in an earlier paper for the preparation of acridine derivatives has been extended and the following compounds have been

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[15] Meisenheirner, *Ann.*, 464, 220 (1926).

[16] Jensen and Homberger, THIS JOURNAL, 48, 800 (1926).

prepared: 1(9)-methoxy-acridine, 1(9)-hydroxy-acridine, 3(7)-ethoxy-acridine, 3(7)-hydroxy-acridine, 5-methyl-acridine, 5,3(7)-dimethyl-acridine, 5-methyl-3(7)-nitro-acridine, 5-phenyl-1(7)-nitro-acridine, 5-phenyl-3(7)-nitro-acridine, 5-phenyl-3(7)-methyl-acridine, 5-phenyl-3(7)-ethoxy-acridine and 5-phenyl-3(7)-hydroxy-acridine.

It has been shown that the chlorine in 5-nitro-2-chloro-acetophenone is labile enough to react with aniline and with o- and *p*-nitro-aniline.

The preparation of the methyl and ethyl esters of acridine-5-carboxylic acid has been described.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE ACTION OF SODIUM TRIPHENYLMETHYL UPON TRIMETHYLMETHOXYAMMONIUM IODIDE AND OF TRIPHENYLMETHYL HALIDES UPON TRIMETHYLAMINE[1]

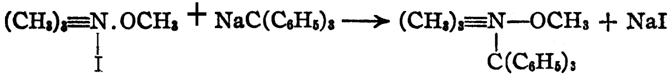
BY LAUDER W. JONES AND MERRILL W. SEYMOUR

RECEIVED SEPTEMBER 27, 1927 PUBLISHED APRIL 6, 1928

The researches of Schlenk and Holz, which led to the preparation of tetramethylammonium triphenylmethyl, $(CH_3)_4N{\cdot}C(C_6H_5)_3$, and tetramethylammonium benzyl, suggested the possibility of synthesizing compounds of a new class similar in type to the isomeric alkylated amine oxides, $R_3N(OR)(OR')$, investigated by Meisenheimer,[2] but differing from them by a substitution of the triphenylmethyl radical for an alkoxy group, for example, $R_3NOR{\cdot}C(C_6H_5)_3$. Isomeric with compounds of this class would be alcoholates of the form $R_3N[C(C_6H_5)_3]{\cdot}OR$. The experiments described below were undertaken with the hope of obtaining derivatives of these types.

I. The Action of Sodium Triphenylmethyl upon Trimethylmethoxyammonium Iodide.—When these two substances were shaken together in very carefully purified ether, the deep red color of the solution changed in time to a pale yellow shade, but no intensely colored compound such as that described by Schlenk as characteristic of tetramethylammonium aryls was noticed; sodium iodide, trimethylamine, triphenylmethane and triphenylethanol were the chief products isolated.

These results suggest that trimethylmethoxyammonium triphenylmethyl was undoubtedly formed in the first stages of the reaction.



$$(CH_3)_3{\equiv}\underset{\displaystyle I}{\underset{|}{N}}.OCH_3 + NaC(C_6H_5)_3 \longrightarrow (CH_3)_3{\equiv}\underset{\displaystyle C(C_6H_5)_3}{\underset{|}{N}}{-}OCH_3 + NaI$$

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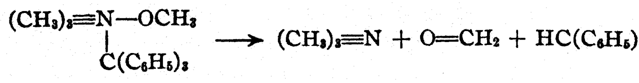
[1] This article is based upon a thesis presented by Merrill W. Seymour to the Faculty of the Graduate School of Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Meisenheimer, Ann.. 397, 273 (1913).

It decomposed at once in the following manner



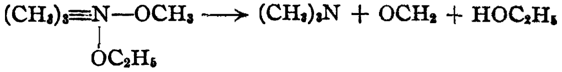
$$\underset{C(C_6H_5)_3}{(CH_3)_3{\equiv}N{-}OCH_3} \longrightarrow (CH_3)_3{\equiv}N + O{=}CH_2 + HC(C_6H_5)_3$$

Formaldehyde is known to react with sodium triphenylmethyl to give sodium triphenylethanol[3]

$$CH_2{=}O + NaC(C_6H_5)_3 \longrightarrow NaO{-}CH_2C(C_6H_5)_3$$

These reactions account for the main products actually isolated.

In many details this decomposition resembles the behavior of the unstable alkylated amine oxides described by Meisenheimer. Thus a solution of trimethylmethoxyammonium ethylate gave trimethylamine, formaldehyde and ethyl alcohol.



$$\underset{OC_2H_5}{(CH_3)_3{\equiv}N{-}OCH_3} \longrightarrow (CH_3)_3N + OCH_2 + HOC_2H_5$$

In our reaction the methoxy group, as it left its position in the molecule, furnished a hydrogen atom (or proton) which ultimately united with the negative ion, triphenylmethyl; thus formaldehyde and triphenylmethane resulted.

II. Attempts to Synthesize Trimethyltriphenylmethyl Ammonium Salts.—Schlubach[4] states that he submitted triethyltriphenylmethyl ammonium iodide, $(C_6H_5)_3C{-}N{\equiv}(C_2H_5)_3{\cdot}I$, to electrolysis in liquid ammonia solution, but he makes no mention of the properties of this substance or the method of its preparation. This is the only reference that could be found in the literature concerning ammonium salts in which one of the radicals attached to nitrogen by a co-valence is triphenylmethyl, unless addition products of triphenylchloromethane to pyridine and to quinoline[5] may be considered as representatives of this type.

In our efforts to obtain salts of this class two procedures were followed, namely, the addition of methyl iodide to dimethylamino-triphenylmethane, and the action of triphenylmethyl halides upon trimethylamine.

Dimethylaminotriphenylmethane and methyl iodide, with and without solvents, showed little tendency to react with each other at room temperature. Some tetramethylammonium iodide was formed, together with a small amount of a dark red, crystalline material which appeared to be partially triphenylmethyl iodide. To account for such a reaction it seems reasonable to assume that some addition of methyl iodide occurred and that the addition product dissociated as follows

$$(C_6H_5)_3C{-}N{=}(CH_3)_2 + CH_3I = (C_6H_5)_3C{-}N{\equiv}(CH_3)_3{\cdot}I$$
$$(C_6H_5)_3C{-}N{\equiv}(CH_3)_3.I = (C_6H_5)_3C{\cdot}I + N(CH_3)_3$$
$$N(CH_3)_3 + CH_3I = N(CH_3)_4{\cdot}I$$

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[3] Schlenk and Ochs, *Ber.*, 49, 610–611 (1916).

[4] Schlubach and Miedel. *Ber.*, 56, 1895 (1923).

[5] Meyer and Fischer, *J. prakt. Chem.*, [2] 82, 523 (1910).

When triphenylchloromethane was treated with trimethylamine in solvents or without solvents at various temperatures and pressures, no addition product could be isolated. Triphenylmethyl bromide behaved similarly. The failure to obtain addition products confirms the earlier experiments of Nef.[6]

Experimental Part

I. The Action of Sodium Triphenylmethyl upon Trimethylmethoxyammonium Iodide.—This iodide was obtained by the action of methyl iodide upon trimethylamine oxide in methanol solution.[7]

A solution of sodium triphenylmethyl in about 600 cc. of carefully purified ether was prepared from 8.52 g. of triphenylchloromethane and an amalgam made with 1.8 g. of sodium and 90 g. of mercury.? A reaction tube similar in form to that described by Schlenk[9] was used. All operations were carried out in an atmosphere of nitrogen. After the tube had been charged and sealed, it was shaken for twelve hours in a dark room. The tube was then opened in an atmosphere of nitrogen and the sodium chloride was separated by filtration of the liquid through a dried Soxhlet thimble in a stream of nitrogen with an apparatus similar to that of Schlenk.[10] The filtrate, deep red in color, was collected in a second reaction tube.

At this stage, 3.66 g. of finely powdered trimethylmethoxyammonium iodide, previously dried over phosphorus pentoxide, was mixed with the filtered solution. Some small glass beads were also added. The tube was then sealed and placed in a shaking machine.

After the mixture had been shaken for eighteen hours, the tube contained a pale yellow solution and a fine, flesh-colored precipitate. The solid was collected on a plate in a specially constructed filtering apparatus through which a stream of nitrogen could be passed. The filter flask was connected with two gas wash bottles containing dilute hydrochloric acid and these in turn were connected with a pump. This precaution was necessary to absorb any trimethylamine which might be carried over in the stream of gas. After filtration the ether filtrate was shaken with the hydrochloric acid solution from the two wash bottles and then washed with water.

In this way the products of reaction were distributed into three parts: (1) a solid, (2) a hydrochloric acid solution, (3) an ether solution.

1. The Solid

The solid was washed with ether. Benzene dissolved only 0.01 *g.* The residue weighed 3.21 g. It was dissolved in 250 cc. of water and 10 cc. portions were analyzed for sodium, for iodine ion, sodium as sodium sulfate and iodine as silver iodide. The amount of hydroxyl ion was determined by titrating 20 cc. of the water solution over 0.1 N HCl; 3.63 cc. of acid was required. These results showed sodium ion, 0.0252 g.; iodine ion, 0.0182 g.; hydroxyl ion, 0.0045 g. This corresponds to 2.73 g. of sodium iodide; calculated amount, 2.53 g.

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[6] Nef, *Ann.*, 309, 168 (1899).

[7] (a) Dunstan and Goulding, *J. Chem. Soc.*, 75, 797 (1899); (b) Meisenheimer, *Ann.*, 397, 288 (1913).

[8] Schlenk and Ochs, *Ber.*, 49, 609 (1916).

[9] Schlenk, *Ber.*, 46, 2843 (1913), Fig. 1.

[10] Schlenk, *Ber.*, 46, 2844–2845 (1913), Figs. 2 and 3.

2. The Hydrochloric Acid Solution

The acid solution was evaporated to dryness. The residue, 1.49 g., was recrystallized by dissolving it in warm chloroform and precipitating it with ether. The purified crystals, identified as trimethylammonium chloride, weighed 1.28 g.; calculated amount, 1.49 g.

3. The Ether Solution

After complete evaporation of the ether, a white solid together with a yellow oil was obtained; weight, 7.2 g. The residue was treated carefully with small amounts of dry ether which dissolved the oil and a portion of the crystals. The remaining crystals, collected and dried, weighed 0.95 g.; m. p. 202°.

The ether solution was evaporated and, by a laborious process of crystallization, the semi-solid residue was resolved into two main fractions consisting of triphenylmethane and triphenylethanol. It was observed that triphenylmethane separated from alcoholic solutions of mixtures containing triphenylethanol, and that triphenylethanol could be freed from small amounts of triphenylmethane by crystallization from ligroin. By combining the crops of crystals of similar melting points and working up the mother liquors, it was possible finally to obtain 2.26 g. of triphenylmethane, m. p. 91–92'; calculated amount, 4.12 g. These crystals mixed with pure triphenylmethane showed a melting point of 92–93".

The second fraction consisted of 0.49 g. of impure triphenylethanol melting at 96°; calculated amount, 3.75 g. Mixed with pure triphenylethanol the melting point was 100–105°. Recrystallization of the solid from ligroin caused the melting point to rise to 104–105°. Triphenylethanol melts at 106–107°.

In addition to these two compounds, about 0.18 g. of colorless material melting at 183–185°, and 0.038 g. melting at 180–185" were obtained. These crystals and the crystals (0.95 g.) melting at 202" probably consisted chiefly of polymers of triphenylmethyl or their peroxides. They were not positively identified.

Since the difficult separation of triphenylmethane from triphenylethanol was accompanied by loss of material at each step, the low values found for triphenylmethane and triphenylethanol are not surprising. Residual oils which could not be solidified undoubtedly contained both of these substances; only the solid crystals of practically pure substances were weighed,

Preparation **of Triphenylethanol.**—The method of Schlenk and Ochs[3] was modified; solid para-formaldehyde was used in place of formaldehyde gas. A solution of sodium triphenylmethyl in ether was prepared from 2.95 g. of triphenylchloromethane and an amalgam made from 4.52 g. of sodium and 6.8 g. of mercury. The solution was filtered into a second reaction tube in a stream of dry nitrogen.

Paraformaldehyde, 0.35 g., previously dried over phosphorus pentoxide, was added, the tube was sealed and placed in a shaking machine. After forty-two hours the color of the solution was pale yellow. The tube was opened and the ether washed with water. After drying the ether, it was distilled. A pale yellow oil remained which gradually deposited crystals. The solid, purified by slow crystallization from ligroin (70–80°), gave large, transparent crystals; m. p. 106–107°. In all 1.44 g., about 50% of the calculated amount, was obtained.

II. Attempts to Prepare Trimethyltriphenylmethylammonium Salts. Preparation **of Dimethylaminotriphenylmethane.**—Hemilian and Silberstein[11] prepared this substance by passing dimethylamine gas through a solution of triphenylbromomethane in benzene. The method employed by us makes use of triphenylchloromethane and is more saving of dimethylamine.

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[11] Hemilian and Silberstein, *Ber.*, 17, 746 (1884).

A solution of 15.7 g., of triphenylchloromethane in 60 cc. of benzene was placed in a large glass tube cooled by ice. Then 8 g. of liquid dimethylamine, previously cooled by ice and calcium chloride, was poured into the tube. The tube was sealed and shaken in a shaking machine.

After a few days the benzene solution was filled with crystals. The tube was opened and the contents shaken with water. The benzene layer was dried and the benzene distilled. The residue gradually gave crystals which increased in amount when a little ethyl alcohol was added. After purification of the substance by recrystallization from absolute alcohol, it melted between 95 and 97°; yield, 10.3 g. or 65% of the calculated amount.

Action of Methyl Iodide upon Dimethylaminotriphenylmethane.—No reaction occurred when dimethylaminotriphenylmethyl and methyl iodide were brought together at room temperature.

In one experiment, 2.88 g. of dimethylaminotriphenylmethane was dissolved in 20 cc. of methyl iodide and this solution was heated for two hours in a sealed tube placed in a bath of boiling water. The tube was opened and the contents treated with ether and chloroform. A dark reddish solid weighing 1.52 g. remained. This solid was washed with chloroform and dried. The dry crystals had a brownish color. Hot ethyl alcohol removed the color. They did not melt at 280° but appeared to sublime below that temperature.

Anal. Subs., 0.1226: AgI, 0.1417. Calcd. for $(CH_3)_4NI$: I, 63.13. Found: 62.50.

The chloroform extracts evaporated to dryness gave a dark red solid which was recrystallized from alcohol. This yielded impure red crystals soluble in boiling ligroin. They probably contained triphenylmethyl iodide. This was not definitely established.

All attempts to add triphenylmethyl chloride or bromide to trimethylamine failed. Reactions were tried with and without solvents and at various temperatures. Invariably the triphenylmethyl halide was recovered, practically quantitatively. Usually a very small amount of a trimethylammonium salt was formed but this undoubtedly was produced by slight hydrolysis of the triphenylmethyl halide.

Summary

1. When sodium triphenylmethyl reacted with trimethylmethoxyammonium iodide, the chief products formed were trimethylamine, triphenylmethane, triphenylethanol (by secondary reaction from formaldehyde) and sodium iodide. It is assumed that the primary product of the reaction was trimethylmethoxyammonium triphenylmethyl which decomposed.

2. All attempts to add triphenylmethyl halides to trimethylamine or methyl iodide to dimethylaminotriphenylmethane were unsuccessful.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

BENZALCREATININE AND RELATED COMPOUNDS

BY BEN H. NICOLET AND EDWARD D. CAMPBELL[1]

RECEIVED SEPTEMBER 30, 1927 PUBLISHED APRIL 5, 1928

Creatine and creatinine have recently[2] become much more available for synthetic work. As one of us[3] has shown the suitability of the condensation products of glycocyamidines with benealdehyde as tools in the study of the methylation of glycocyamidine, it seemed desirable to attempt to extend this method to creatinine derivatives. It also seemed likely that the aldehyde condensation products of creatinine might provide a convenient means of obtaining a-methylamino acids.

Although the alkylation of glycocyamidine and of creatinine has received considerable attention, the two methods of proof that have been offered for the structures of the derivatives obtained seem to be quite without value. For a detailed discussion of this point, reference may be made to the paper by Johnson and Nicolet already cited.

An outline of the synthetic work involved may well accompany the discussion of its application to these problems. The method of Erlenmeyer, Jr.,[4] for the preparation of acetyl-5-benzalcreatinine (I)[5,6] was improved to give an 80% yield. Hydrolysis with acids readily gave 5-benzalcreatinine (11), but (I) may be used directly for many purposes. For instance, reduction (and hydrolysis) of (I) with hydriodic acid (tin and hydrochloric acid can also be used) gave 5-benzylcreatinine (III) in 66% yield.

Intensive hydrolysis of (III) with hot barium hydroxide solution gave N-methylphenylalanine (yield, 44%); the hydrolysis could also be so controlled as to give a good yield of 1-methyl-5-benzylhydantoin (IV),

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[1] The material here presented was used by Edward D. Campbell in partial satisfaction of the requirements for the degree of Doctor of Philosophy at the University of Chicago, **1924.**

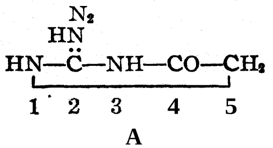
[2] Graham Edgar, *Chem.* Met. *Eng.*, **24, 485 (1922).**

[3] **Johnson** and Nicolet, THIS JOURNAL, 37,2416 **(1915).**

[4] Erlenmeyer, Jr., *Ann.*, **284, 49 (1895).**

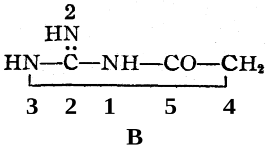
[5] No direct evidence is available for the position assigned to the acetyl group.

[6] The numbering system used here for the glycocyamidine ring is that adopted by *Chemical* Abstracts, and is illustrated in Formula A. Unfortunately a different system



$$\underset{1\quad 2\quad 3\quad 4\quad 5}{\mathrm{HN{-}\overset{\overset{N_2}{HN}}{\ddot{C}}{-}NH{-}CO{-}CH_2}}$$

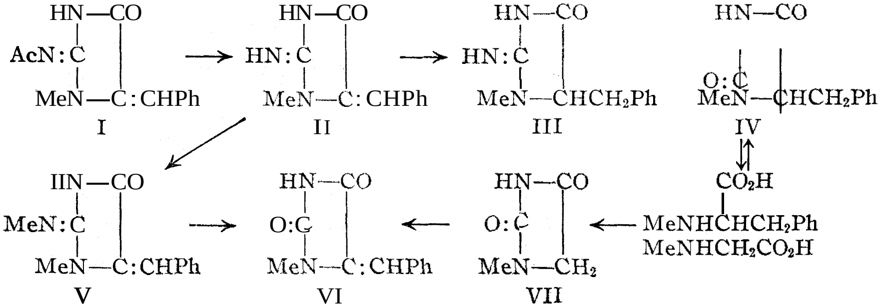
A



$$\underset{3\quad 2\quad 1\quad 5\quad 4}{\mathrm{HN{-}\overset{\overset{2}{HN}}{\ddot{C}}{-}NH{-}CO{-}CH_2}}$$

B

(Formula **B)** has been used in many publications, particularly in the numerous publications of Johnson and his co-workers, so that one must guard against confusion of names.



which was also synthesized from methylphenylalanine for comparison. The isolation of (IV), rather than the corresponding hydantoic acid, in this gentler hydrolysis, although no acid stronger than carbonic acid was used in working up the product, indicates that the hydrolysis took place without opening of the ring.

The preparation of N-methylphenylalanine just described gives an over-all yield of 22% from creatine in three steps. Considering the present availability of the starting material, this procedure may be found to compare favorably with the other methods available.[7] There seems little doubt that equal success would be attained in the use of other aromatic aldehydes in the preparation of analogous methylamino acids.[8]

The methylation of (II) with methyl iodide and alkali gave the methylbenzalcreatinine (V), the structure of which seems to follow definitely[9] from the fact that hydrolysis converted it nearly quantitatively to 1-methyl-5-benzalhydantoin (VI), with the liberation of methylamine apparently unaccompanied by any ammonia. The formation of (V) was unexpected, since the analogous alkylation of 5-benzalglycocyamidine resulted[3] in the formation of 3-methyl-5-benzalglycocyamidine. It seems, however, to be well established that it is a matter of somewhat extreme difficulty to open the ring in any of the unreduced aldehyde condensation products of hydantoins or of glycocyamidines by the action of alkali and, on the other hand, fairly intensive action of acids is in general necessary to close such rings. We therefore do not consider the evidence here offered for the structure of this derivative as open to the same ob-

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[7] (a) Friedmann and Gutmann, Biochem. *Z.*, **27**, 491 (1911); (b) Fischer and Lipschitz, Ber., 48,360 (1915).

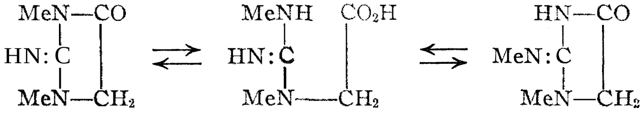
[8] Johnson and Nicolet, *Am. Chem. J.*, **47**, 459 (1912), recommended the synthesis of such compounds from hydantoin, and used N-methyltyrosine as an illustration. The substitution of creatine for hydantoin as a starting material eliminates the necessity for the introduction of two methyl groups.

[9] There is one bit of contrary evidence, The substance (V) is practically insoluble in cold aqueous alkali, which would suggest replacement of the hydrogen in position 3; but benzalcreatinine is itself only slightly soluble under the same conditions, and the evidence based on hydrolysis accordingly appears to us conclusive.

jections as have been raised[a] against the use, in otherwise similar cases, of evidence of structure from the alkaline hydrolysis of the glycocyamidine derivatives themselves.

The identity of (VI) was confirmed by its synthesis from the 1-methylhydantoin (VII) prepared from sarcosine. It was also obtained by the hydrolysis of (I) or (II).[10]

The methylation of creatinine by the method used by Korndörfer[11] and by Kunze[12] gave a methylcreatinine (VIII) or (IX) with the properties described by them. Unfortunately, all efforts to condense this product with benzaldehyde for comparison with (V) failed. As it has been shown[13] that N²-methylglycocyamidine, when the ring is opened by treatment with alkali and then closed again by digestion with acid, gives a considerable amount of the isomeric 3-methylglycocyamidine, and as there was still reason to hope that at least one of the methylcreatinines would be capable of condensation with benzaldehyde, an attempt was made to "rearrange" our methylcreatinine in the sense indicated:



VIII IX

The product obtained after opening and again closing the ring still failed to condense with benzaldehyde under any of the conditions tried. It was, therefore, impossible to obtain any direct evidence as to the structure of the methylation products of creatinine itself by the method planned.

The failure of the methylcreatinines to undergo condensation, while rather unexpected, is not at all without precedent. Thus, Wheeler and Hoffman[14] obtained easy condensation with 3-phenylhydantoin, but none at all with the 1-phenyl and 1,3-diphenyl derivatives. Similarly, Biltz[15] was unable to carry out the reaction with 1,3-dimethylhydantoin, and in the case of 1-methylhydantoin we obtained less than half the usual yield. For some reason not yet adequately understood the accumulation of substituents on the nitrogens interferes more or less completely with this type of condensation.

[10] This hydrolysis method is the best available for the preparation of 1-methylated aldehyde condensation products of hydantoin, as these derivatives cannot be directly alkylated in position 1 until after the hydrogen in position 3 is replaced. On the other hand, 1-methylhydantoin requires sarcosine for its synthesis, and gives poor yields on subsequent condensation.

[11] Korndorfer, *Arch. Pharm.*, **242,** 641 (1904).

[12] Kunze, *ibid.*, **248, 578** (1910).

[13] Ref. 3, p. 2426.

[14] Wheeler and Hoffman, *Am. Chem. J.*, **45, 368** (1911).

[15] Biltz, *Ber.*, **45,** 1673 (1912).

Experimental Part

N-Acetyl-5-benzalcreatinine (I).—A mixture of 5 g. of creatine, 4 g. of benzaldehyde, 15 g. of fused sodium acetate, 50 cc. of glacial acetic acid and 15 cc. of acetic anhydride was refluxed in an oil-bath for an hour and the warm solution then poured into 1 liter of water. Seven grams (80%) of the acetyl-benzalcreatinine separated. It formed golden yellow needles from alcohol and melted at 208–209°. The same product was obtained in smaller yield by the method of Erlenmeyer, Jr.,[4] but his m. p. of 213° could not be attained.

Anal. Calcd. for $C_{13}H_{13}O_2N_3$: N, 17.28. Found: 17.19, 17.38, 17.27.

Dihydrochloride of **5-Benzalcreatinine.**—The acetyl derivative was digested for two hours with an excess of 30% hydrochloric acid on the steam-bath and the solution then evaporated to dryness. From water containing a considerable amount of hydrochloric acid. the product separated in bright yellow crystals as the dihydrochloride.

Anal. Calcd. for $C_{11}H_{11}ON_3.2HCl$: N. 15.33. Found: 15.67, 15.82.

A portion of the second mole of hydrochloric acid is very easily lost by hydrolysis.

5-Benzalcreatinine (II).—The hydrochloride was dissolved in 40 parts of water and precipitated with excess of ammonium hydroxide. The product crystallized from alcohol in yellow flakes which darkened near 225° and melted with effervescence at 244°. It retained water tenaciously.

Anal. Calcd. for $C_{11}H_{11}ON_3$: N, 20.89. Found: 20.62, 20.51.

5-Benzylcreatinine (III).—Five grams of acetylbenzalcreatinine, 2 g. of red phosphorus, and 25 cc. of hydriodic acid (sp. gr. 1.7) were boiled for five hours under reflux; 6.8 g. of iodine was then added and boiling continued for five hours. The solution was evaporated nearly to dryness, the residue extracted with 100 cc. of hot water, and the resulting solution filtered. Concentration and cooling of the filtrate caused almost no separation of solid. Ammonium hydroxide in excess precipitated 2.9 g. (66%) of benzylcreatinine. From the filtrate 0.3 g. additional could be isolated, but this is not recommended. The substance crystallized from alcohol or water in white flakes melting with some decomposition at 282°.

Anal. Calcd. for $C_{11}H_{13}ON_3$: N, 20.68. Found: 20.54, 20.68.

The same substance was obtained when acetylbenzalcreatinine was boiled for six hours with 40 parts of 20% hydrochloric acid and a three-fold excess of tin. The solution was evaporated nearly to dryness, the residue taken up in 100 cc. of boiling water, excess of ammonium hydroxide added, and the solution filtered hot from precipitated tin compounds. The filtrate yielded benzylcreatinine (52%).

Hydrolysis of **5-Benzylcreatinine; N-Methylphenylalanine.**—In an apparatus similar to that used for Kjeldahl distillations, except that provision was made for the continuous addition of water to replace that which distilled, 5 g. of benzylcreatinine and 40 g. of barium hydroxide in 50 cc. of water were boiled for ten hours. The ammonia, which was evolved continuously, was collected in standard acid, and at this time amounted to 2 molar proportions for the material used. The reaction mixture was diluted to 400 cc., and carbon dioxide was passed in until no more barium carbonate precipitated. When the solution was filtered and the filtrate concentrated to 10 cc., 1.8 g. of N-methylphenylalanine separated on cooling as clusters of fine, white needles. It sublimed with very little decomposition at 252–254°.[16]

Partial Hydrolysis **of** 5-Benzylcreatinine; **1-Methyl-5-benzylhydantoin** (IV).—Using the same apparatus as in the preceding hydrolysis, 5 g. of benzylcreatinine was

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[16] Friedmann and Gutmann, *Biochem. Z.*, 27, 491 (1910), also report sublimation with slight decomposition, 252–254°.

heated with 3 g. of barium hydroxide in 50 cc. of water until 1 molar proportion of ammonia had collected in the distillate (four hours). The mixture, worked up as before, gave 3.0 g. of 1-methyl-5-benzylhydantoin, which after purification melted at 106°.

Anal. Calcd. for $C_{11}H_{12}O_2N_2$: N, 13.72. Found: 13.63, 13.80.

The same substance was prepared in 50% yield by the action of potassium cyanate on an acidified solution of N-methyl phenylalanine and subsequent digestion with hydrochloric acid. A mixture of the two products also melted at 106°.

1-Methyl-5-benzalhydantoin (VI).—By a similar hydrolysis procedure, 5 g. of acetylbenzalcreatinine and 35 g. of barium hydroxide in 50 cc. of water required ten hours' boiling for the evolution of 1 mole of ammonia. The solution yielded 4.0 g. of 1-methyl-5-benzalhydantoin as light yellow flakes melting at 193–194°.

Anal. Calcd. for $C_{11}H_{10}O_2N_2$: N, 13.87. Found: 13.66, 13.88, 13.70.

When sarcosine was converted to 1-methylhydantoin (m. p. 156°) and the latter condensed with benzaldehyde by the usual method, the same substance was obtained. A mixture of the two products also melted at 193–194°. It is of interest that, in three experiments, the average yield of benzal derivative from 1-methylhydantoin was only 32%.

1,3-Dimethyl-5-benzalhydantoin.—The methylation of 2 g. of 1-methyl-5-benzalhydantoin with methyl iodide and sodium hydroxide in hot alcohol gave 1.0 g. of the dimethyl derivative, which, recrystallized from hot water, melted at 92°. It was not soluble in aqueous alkali.

N^2-Methyl-5-benzalcreatinine (V).—A solution of 5 g. of benzalcreatinine, 1.1 g. of sodium hydroxide and 5 g. of methyl iodide in 200 cc. of alcohol was heated until it became neutral (ten hours) and then evaporated to dryness. Extraction with 300 cc. of cold 5% sodium hydroxide solution dissolved 1.8 g. of unmethylated benzalcreatinine, which separated on acidification. The residue, insoluble in cold alkali, was crystallized from hot water and gave 2.9 g. of methylbenzalcreatinine as light yellow flakes melting at 129°.

Anal. Calcd. for $C_{12}H_{13}ON_3$: N, 19.53. Found: 19.75, 19.62.

The same product was obtained when 1.5 g. of benzalcreatinine, 1.3 g. of methyl iodide and 3 cc. of methyl alcohol were heated for three hours at 100° in a bomb tube. In this case no alkali-soluble material remained.

Hydrolysis of N^2-Methyl-5-benzalcreatinine.—When a solution of 6 g. of the methylated benzalcreatinine just described and 40 g. of barium hydroxide in 60 cc. of water was boiled for two hours, 1 mole of amine appeared in the distillate. This was shown to be methylamine by its practically quantitative conversion to dimethyloxamide. No oxamide which would indicate the initial presence of ammonia could be detected

The hydrolysis mixture was diluted with water and filtered hot. The filtrate, after removal of barium salts and concentration, gave 0.1 g. of 1-methyl-5-benzalhydantoin. The original insoluble portion was treated with warm dilute hydrochloric acid until solution was complete; excess of ammonium hydroxide then precipitated 4.5 g. of the methylbenzalhydantoin.

Methylation of Creatinine.—A mixture of 2 g. of creatinine, 2.6 g. of methyl iodide and 3 cc. of methyl alcohol (when the latter was omitted practically no reaction took place) was heated in a bomb tube for three hours at 100°. When the resulting solution was slightly concentrated, 2.0 g. of methylcreatinine hydriodide separated. This salt crystallized from alcohol in pale yellow needles which melted at 211–212°, and was presumably identical with the product similarly obtained by Korndörfer[11] and by Kunze.[12]

This salt was dissolved in water and shaken with an excess of precipitated silver chloride. The methylcreatinine hydrochloride thus obtained melted with slight decomposition at 234–236°, as reported. All attempts to condense this product with benzaldehyde, either by the usual procedure or with longer heating and increased proportions of sodium acetate and of acetic anhydride, were completely unsuccessful.

At this stage it was thought worth while to show that the methylation could not have taken place with the introduction of a second methyl group on the 1-nitrogen. The methylcreatinine was accordingly hydrolyzed and found to yield sarcosine and methylamine. Since it was thus clear that the substance must have one of the two structures represented by VIII and IX, it was sought to convert it into *a* mixture of these two isomers (see discussion) in the hope that at least one of them might be condensed with benzaldehyde. The mixture obtained, however, gave no benzal derivative.

Summary

1. Benzalcreatinine and a number of new compounds derived from it have been described.
2. N-Methylphenylalanine may conveniently be prepared by the reduction and subsequent hydrolysis of benzalcreatinine.
3. Methylation of benzalcreatinine takes place first on the nitrogen atom in position 2. N-Methylcreatinine does not condense with benzaldehyde.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

THE POLYMERIZATION OF INDENE, CINNAMAL FLUORENE AND SOME DERIVATIVES OF INDENE

BY GEORGE STAFFORD WHITBY AND MORRIS KATZ

RECEIVED NOVEMBER 12, 1927 PUBLISHED APRIL 5, 1928

Indene is known to be polymerizable by concentrated sulfuric acid, heat and other means.[1] The polymerizing agencies used in the present work were heat, antimony pentachloride and stannic chloride. The two latter were found to yield polymers higher than any previously obtained.[2] The molecular weight of the $SbCl_5$ product corresponded approximately to that of a molecule derived by the union of 15 indene molecules, while that of the $SnCl_4$ product corresponded approximately to the union of 25 indene molecules. Although these polymers are thus comparatively high, they do not show the properties of lyophilic colloids. Further, they do not represent chemical individuals but, rather, as was shown by fractionation, mixtures representing widely different degrees of polymeri-

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[1] (a) Krämer and Spilker, *Ber.*, **23**, 3276 (1890); (b) **33**, 2260 (1900); (c) Weger, *Z. angew. Chem.*, **22**, 345 (1909); (d) Weger and Billmann, *Ber.*, **36**, 640 (1903); (e) Weissgerber, *Ber.*, 44, 1438 (1911); (f) Guntz and Minguin, Comfit. *rend.*, **152**, 373 (1911); (g) Ciamician and Silber, *Ber.*, **46**, 420 (1913); (h) Stobbe and Färber, *Ber.*, **57**, 1838 (1924); (i) Staudinger, *Ber.*, 59,3019 (1926); (j) Bruson, *Diss.*, Zürich (1925); (k) *Ber.*, *60*, 1094 (1927).

[2] Since the present work was complete some data on the polymeric product obtained from indene by $SnCl_4$ have been published by Staudinger, ref. 1 i.

zation.[3] From the $SnCl_4$ product there was obtained at one extreme a fraction $(C_9H_8)_8$ and at the other a fraction $(C_9H_8)_{29}$.

The polymerization of indene by heat was followed at various temperatures and was found to take place the more rapidly the higher the temperature. At a given temperature, the molecular weight of the product was found to rise as the proportion of the indene which had undergone polymerization increased. The molecular magnitude ultimately attained when polymerization had become substantially complete appeared to be lower, the higher the temperature employed. Thus, at 200°, when polymerization was 96.75% complete, the molecular weight was 676, whereas at 178°, when polymerization was only 82.24% complete, it was 886.[4] The explanation of the fact that the higher the temperature at which polymerization is brought about, the lower is the molecular weight of the product ultimately obtained, is not improbably similar to that which Staudinger[1i] has suggested in the case of styrene, namely, that "cracking" sets a limit to the size of polymeric molecule which can exist at a given temperature.

Like the $SbCl_5$ and $SnCl_4$ polymers, the heat polymers are heterogeneous.

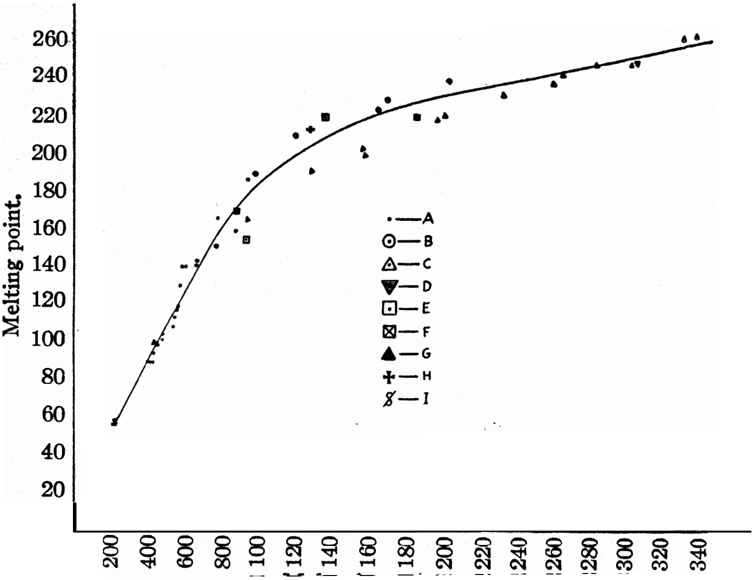
There is a clear relationship between the melting points and molecular weights of the polyindenes, the former rising regularly with increase in the latter. Fig. 1 shows the data in this connection for all the 39 samples of polyindene described in the experimental part. The relation between melting point and molecular weight can hardly be expected to be very close in view of the errors attendant on the determination of the high molecular weights and of the fact that the products are amorphous mixtures. There has also been included in the figure points representing products described by previous workers, namely, a dimer,[1h] three thermo-polymers,[1h,k,j] two photo-polymers,[1h] and a sulfuric acid polymer.[1j] These all agree reasonably well, considering the circumstances, with the relationship found for the products of the present investigation. It would appear that the polymers of indene, no matter by which of the known means they are produced, form a regular and unbroken series, increasing in melting point with increase in the degree of polymerization.

Fifteen samples of polyindene (7 by $SnCl_4$, 8 by heat), the bromine absorption of which was measured, all showed substantially the same degree of unsaturation per molar weight, namely, that represented by the absorption of two atoms of bromine. Hence all the polyindene molecules, no matter what their size, contain one double bond.

[3] Products of the polymerization of indene to which authors have assigned names carrying the suggestion that the products are chemical individuals (see refs. 1 c and 1 k) are, in the light of the present investigation, almost certainly mixtures.

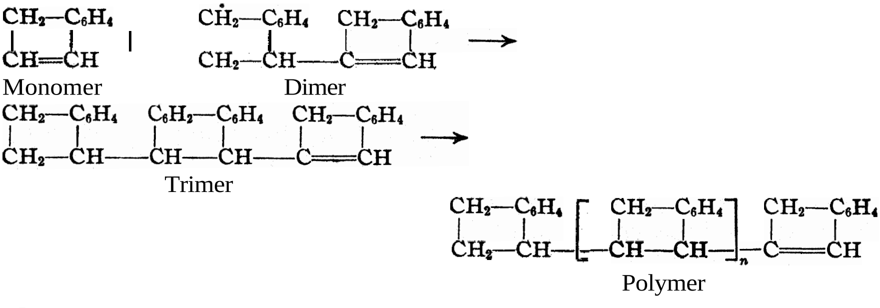
[4] At 260° a product with a molecular weight of 467 was obtained by Bruson (ref. 1 k) by heating for 25 hours—a period sufficient, to judge by the present investigation, for complete polymerization.

In the light of these facts the polymerization of indene is best represented as proceeding step-wise by the addition regularly of successive molecules of monomer to the double bond present at the stage of polymerization immediately preceding, according to a scheme such as the following



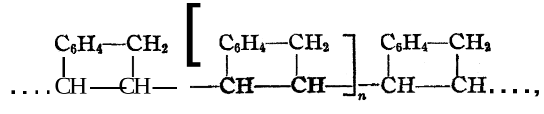
A, Thermo-polymers; B, by $SbCl_5$; C, by $SnCl_4$; D, by $SnCl_4$, Bruson, ref. 1i; E, thermo-polymers, Stobbe and Fiirber, ref. 1h; F, photo-polymers, Stobbe and Farber, ref. 1h; G, thermo-polymers, Bruson, ref. 1k; H, by H_2SO_4, Bruson, ref. 1i; I, di-indene, Stobbe and Fiirber, ref. 1h.

Fig. 1.—Polymers of indene.



There are in all four possible similar schemes involving the wandering of a hydrogen atom from the addendum, but the above is chosen because it accords best with both the facts (a) that the polyindenes decompose largely to indene on dry distillation and (b) that the dimer of indene which has been previously described in the literature,[1h] and which, because of its melting point (see Fig. 1) and its polymerizability,[1h] probably lies on the direct path from indene to the polyindenes, gives α-hydrindone on oxidation.

The mode of formulation of polyindenes suggested by Staudinger,[1i] namely,



$$\ldots\underset{\mathrm{CH}}{\overset{\mathrm{C_6H_4}}{|}}\!-\!\underset{\mathrm{CH}}{\overset{\mathrm{CH_2}}{|}}\!-\;\left[-\underset{\mathrm{CH}}{\overset{\mathrm{C_6H_4}}{|}}\!-\!\underset{\mathrm{CH}}{\overset{\mathrm{CH_2}}{|}}\!-\right]_n\!-\underset{\mathrm{CH}}{\overset{\mathrm{C_6H_4}}{|}}\!-\!\underset{\mathrm{CH}}{\overset{\mathrm{CH_2}}{|}}\ldots,$$

which represents the polymerization as due to the coming together of a number of monomeric molecules without the wandering of hydrogen atoms, is out of accord with the fact that the polyindenes are unsaturated, see above, since the free terminal valencies shown in such a method of formulating polymeric products are, on account of the size of the molecule, not regarded as conferring unsaturation.[5] Further, in the case of the lower polymers of indene which are obtained by means of heat and which may contain as few as four indene molecules, such a structure could hardly be stable: it would almost certainly undergo rearrangement to a structure containing an ethylene linkage.

A considerable number of cinnamal compounds have been shown to be photo-polymerizable to dimers.[6] In the present investigation it has been found that the hydrocarbons cinnamal fluorene (I) and cinnamal indene (II) are capable of yielding higher, albeit non-colloidal, polymers.

I

II

Cinnamal fluorene has been stated by Ostromislenski[7] to yield when heated in boiling acetic acid a polymeric product which shows elastic properties; which, when stretched and then released, slowly retracts partially during one or two days. The present authors were unable to secure polymerization of cinnamal fluorene by treatment with acetic acid at any temperature, and the polymers obtained by other means were entirely lacking in elasticity. Heating it alone at 200° for two to three weeks was found to convert cinnamal fluorene into a low polymer, and at 240–250° for three days into a higher polymer corresponding approximately in mean molecular weight to a nonamer. Antimony pentachloride produced a polymer corresponding approximately to an octamer. Fractionation showed the material to be a mixture. Similarly, cinnamal

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[5] Staudinger, *Ber.*, 53, 1073 (1920); Staudinger and Fritschi, *Helv. Chim. Acta*, 5, 787 (1922).

[6] See, for example, (a) Riiber, *Ber.*, 35, 2414 (1902); (b) 46, 338 (1913); (c) Ruhemann, *J. Chem. Soc.*, 85, 1453 (1904); (d) Reimer, *Am. Chem. J.*, 45, 417 (1911); (e) Stobbe, *Ber.*, 45, 3396 (1912); (f) *J. prakt. Chem.*, 110, 129 (1925).

[7] Ostromislenski, *J. Russ. Phys.-Chem. Soc.*, 47, 1374 (1915).

indene was polymerized by heat, by $SbCl_5$ and by $SnCl_4$, and the products were shown to be heterogeneous. Figs. 2 and 3 show that there is a linear relation between the melting point and the molecular weight of the polymers both in the case of cinnamal fluorene and cinnamal indene.

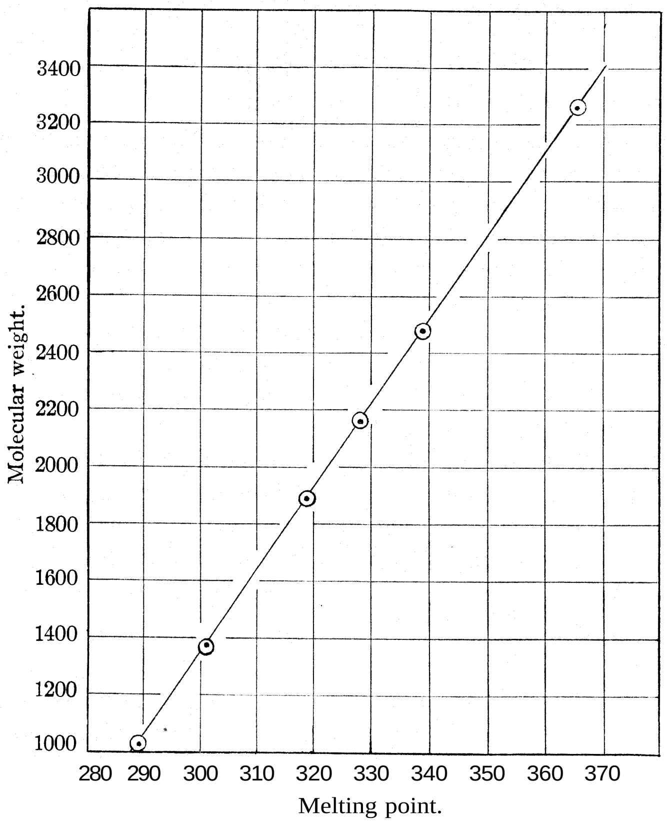
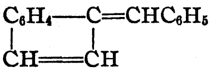


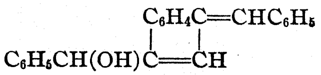
Fig. 2.—Polymers of cinnamal fluorene (by $SbCl_5$).

Other compounds investigated were benzal indene (III) and hydroxybenzyl indene (IV).



$$\begin{array}{ll} C_6H_4 — & C{=}CHC_6H_5 \\ | & | \\ CH{=}{=} & CH \end{array}$$

(III)



$$\begin{array}{rl} & C_6H_4C{=}CHC_6H_5 \\ & | \quad | \\ C_6H_5CH(OH) & C{=}CH \end{array}$$

(IV)

Each of the substances with the polymerization of which the present communication deals contains a conjugated system although, except in the case of the cinnamal compounds, it is not of the typical, open-chain kind. In indene the conjugated system, the presence of which is clearly shown by the magnetic rotatory power,[8] is of what may be called

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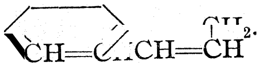
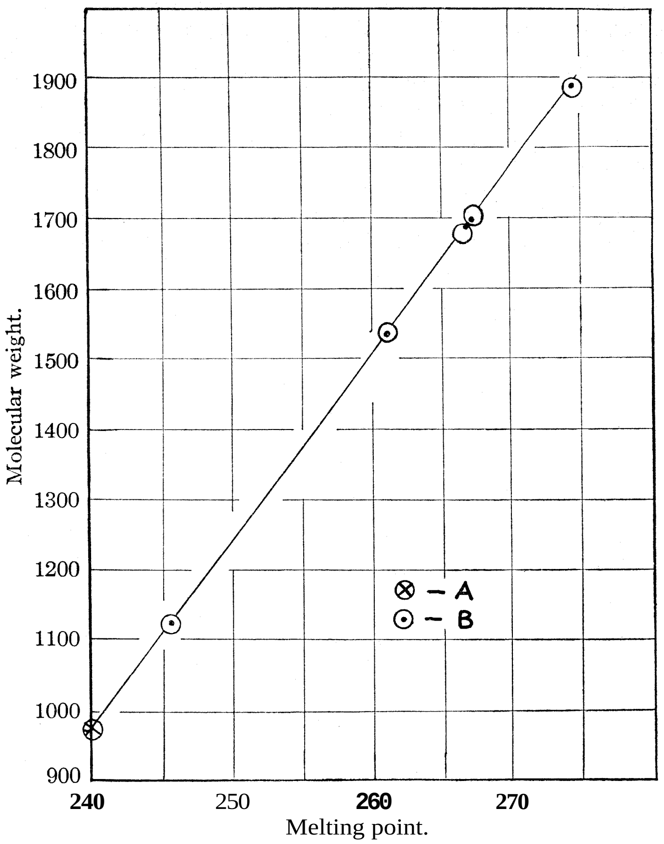
[8] Smiles, "The Relation between Chemical Constitution and Some Physical Properties," Longmans Green and Co., London, 1910, p. 489.

the semi-benzenoid type shown in the following formulation:  In this connection it may be mentioned that preliminary experiments have shown that isoeugenol and isosafrole, both of which, as is proved by physical measurements,[8] contain semi-benzenoid conjugated systems, are polymerizable by $SbCl_5$ and by heating at 200° far more readily than the isomeric compounds, eugenol and safrole, respectively, in which such a system is lacking.[9]



A, $SnCl_4$ polymer; B, thenno-polymers.

Fig. 3.—Polymers of cinnamal indene.

Experimental Part

Indene

The indene used was a pure, colorless sample obtained by several distillations with a fractionating column and boiling at 181–181.5°.

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[9] It is desired to reserve the further investigation of this matter (G. S. W.).

Polymerization by (a) Antimony Pentachloride, (b) Stannic Chloride.—To 10 cc. of indene diluted with an equal volume of chloroform was added 1 cc. of a 20% solution of the chloride in chloroform. The solution became red and warm, a good deal of the chloroform boiling off. After ten minutes it was diluted with 10 cc. more chloroform, and then poured into 100 cc. of absolute alcohol. The precipitated polymeric product was separated, dissolved in benzene and reprecipitated by alcohol, this process being repeated three times. The polyindene thus obtained in quantitative yield as a white powder was free from all traces of the catalyst. A larger batch was prepared in a similar way, starting with 70 cc. of indene and treating with $SnCl_4$. The products were separated into fractions by precipitation with alcohol from benzene solution. In the case of the larger batch of polymer by $SnCl_4$, the last fraction was isolated by removing a considerable proportion of the solvent, adding water, separating the benzene layer and allowing it to evaporate at room temperature. In the case of these and all other polymeric products described herein melting points were taken by the electrically heated apparatus of Mason;[10] molecular weights were determined cryoscopically in benzene unless otherwise stated and the viscosity of 1% solutions in benzene was measured in an Ostwald viscosimeter at 25°. The bromine absorption of seven fractions of the larger batch of polyindene prepared by the aid of $SnCl_4$ was measured by allowing a solution of 1.5–3 g. in 25 cc. of chloroform to stand in the dark for twenty-four hours at room temperature with 25–50 cc. of 0.07 N bromine in chloroform. Preliminary experiments

TABLE I

POLYINDENE BY STANNIC CHLORIDE

First batch

Fraction	M. p., °C.	Mol. wt.	Viscosity (time of flow in secs.)[a]
Before fractionation	247–250	2971	
I	261–264	3254	84.2
2	242–244	2608	81.2
3	217–220	1950	79.0
4	202–204	1558	77.0
5	190–193	1287	74.8

Second batch

Fraction	M. p., °C.	Mol. wt.	Bromine absorption, (atoms per mol.)
1	261–265	3320	2.43
2	247–250	2785	2.06
3	236–241	2560	2.12
4	231–235	2295	1.97
5	219–223	1990	1.85
6	198–201	1568	2.19
7	164–167	952	1.93

Polyindene by $SbCl_5$

Fraction	M. p.. °C.	Mol. wt.	Viscosity (time of flow in secs.)
Before fractionation	228–230	1687	
1	238–240	2013	78.6
2	223–225	1642	76.8
3	209–211	1204	74.2
4	188–191	990	73.0

[a] Time of flow of benzene, 67 secs.; of 1% indent in benzene, 68.6 secs.

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[10] Mason, J. *Soc. Chem. Ind.*, 45, 199 (1926).

had shown that the absorption of bromine was only about 85% complete after four and one-half hours at room temperature but was complete after twenty-four hours. They also showed that indene gave the theoretical amount of absorption by the procedure followed. Data are given in Table I. When dry distilled under a pressure of 2 mm., the $SnCl_4$ polymeric product gave a considerable quantity of indene and also some higher boiling material, which probably consists of low polymers, and which will be further examined.

Polymerization by Heat.—Samples of indene, each about 5 g. in weight, were heated in sealed tubes for various periods at 200, 178, 140 and 100°. The percentage of polymerization was determined by distilling off unchanged indene at 75° under reduced pressure extracting the residue with ether in a Soxhlet in order to eliminate any (insoluble) truxene (no truxene was in fact found in any of the samples), pouring the ether extract into twice its volume of alcohol, collecting the white polyindene and drying it *in vacuo*. The bromine absorption of some of the products was determined by allowing a solution of about 0.8 g. in 25 cc. of chloroform to stand in the dark for twenty-two hours at room temperature with 60 cc. of 0.1 N bromine in chloroform. (Indene in the form of Wijs solution was not absorbed by any of the products.) The following data were obtained.

TABLE II

THERMO-POLYMERIZATION OF INDENE

Period of heating, days	Polymerization, %	M. p. of polymer, °C.	Mol. wt. of polymer	Bromine absorption, atoms per mol.
		At 200°		
1	22.7	103–105	490	
2	38.7	107–109	545	
3	49.1	112–114	553	2.00
4	76.35	128–132	586	1.96
8	89.3	139–142	615	
21	96.75	142–145	676[a]	
		At 178°		
1	5.02	88–90	419	
2	12.4	93–95	442	
3	18.55	97–100	462	
4	26.3	103–105	493	
11	65.5	116–118	566	1.99
16	70.6	140–142	669	2.11
19	74.15	150–152	778	2.11
30	82.2	158–160	886[b]	
		At 140°		
25	15.9	89–90	414	2.03
70	45.35	118–120	574	2.07
		At 100°		
70	2.65			

[a] C, 92.90; H, 7.08.

[b] C, 92.95; H, 7.04 (calcd. for $(C_9H_8)_x$: 93.10, 6.90).

The polymeric product obtained from 10 g. of indene by eight days' heating at 200° was dissolved in 200 cc. of ether and fractionally precipitated by the addition of absolute alcohol in approximately the following amounts: 20, 20, 40, 50 and 75 cc., the precipitate being filtered off after each addition. The following table shows the results obtained.

TABLE III

FRACTIONATION OF THERMO-POLYMERIZED INDENE

Fraction	Before fractionation	1[a]	2	3	4	5
M. p..,..	139–142°	185–188°	165–167"	139–142'	100–102°	88–90"
Mol. wt..	615	948	787	594	491	438

[a] Bromine absorption, 1.94 atoms per mol.

Cinnamal Fluorene

Cinnamal fluorene was prepared according to the directions of Thiele and Henle.[11] It was found that by using absolute alcohol prepared with the aid of calcium instead of commercial absolute alcohol a yield of 25 g. from 40 g. of fluorene was obtained instead of 18–21 g. as mentioned by Thiele and Henle; m. p. 155.5' (from benzene).[12]

Thermo-polymerization.—(a) Solutions of 3 g. of cinnamal fluorene in 50 cc. of liquid were heated at the boiling point in each of the following solvents: toluene (110°), acetic acid (118°), xylene (140°) and tetrahydronaphthalene (207°) for periods ranging in each case from twelve hours to two weeks. In no case was there any evidence of polymerization, the melting point of the material in solution being 155° in every case. (b) Solutions of 5 *g.* of cinnamal fluorene in 25 cc. of acetic acid were heated in sealed tubes at 125° and at intervals of 10° up to 175° for periods in each case up to one week. In every case only unchanged cinnamal fluorene could be recovered. (c) Samples of cinnamal fluorene heated alone for one week at temperatures up to 190° showed no polymerization. After heating at 200° for three weeks a small amount of polymerization occurred and by solution in benzene followed by precipitation with absolute alcohol, there was obtained a red-brown, amorphous powder; m. p., 168–170°; mol. wt., 570 (calcd. for $(C_{22}H_{16})_2$: 560). (d) Cinnamal fluorene was heated in a sealed tube at 240–250° for three days; the product was dissolved in a large volume of benzene and the reddish powder which came out on cooling was collected and dried in *vacuo;* m. p., 356–370°; mol. wt. (Rast's method in camphor), 2558; C, 93.90; H, 5.74 (calcd. for $(C_{22}H_{16})_9$: 2520, 94.28, 5.72). The product was soluble in cold benzene, in chloroform and in carbon tetrachloride with difficulty; more easily soluble in hot benzene and in acetone; insoluble in alcohol, ether, acetic acid and petrolic ether. Like the other polymeric products obtained from cinnamal fluorene, it gave deep red solutions. (Solutions of unpolymerized cinnamal fluorene are yellow.) When dry distilled it yielded cinnamal fluorene.

Polymerization by Antimony Pentachloride.—To a solution of 10 g. of cinnamal fluorene in 250 cc. of chloroform was added 12 cc. of a 20% solution of $SbCl_5$ in chloroform. The solution turned violet in color, then deep blue and became warm. After

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[11] Thiele and Henle, *Ann.*, **347,** 303–304 (1906).

[12] A red, somewhat sticky by-product formed during the condensation of fluorene and cinnamic aldehyde was examined, after being freed from cinnamal fluorene by means of acetone, in which it was more soluble than cinnamal fluorene. This material could be stretched, and it seems possible that it was a similar product that Ostromislenski (ref. 7) described as an elastic polymer of cinnamal fluorene. Although the material could be stretched, it showed no elasticity, as it entirely failed to retract after being extended. It was soluble in hot alcohol and was not improbably a condensation product of two molecules of cinnamic aldehyde, because (a) the molecular weight was 276, and (b) a similar red, amorphous product could be prepared by treating cinnamic aldehyde with sodium ethylate in the absence of fluorene.

standing for four hours, it was poured into 500 cc. of absolute alcohol, which decomposed the complex addition product and caused separation of the polymer. The latter was collected, dissolved in benzene and reprecipitated with alcohol. This purification was repeated four times and the final product, consisting of a dark yellow powder free from catalyst, was dried in *vacuo;* yield, 8.2 g.; m. p., 327–329°; C, 93.89; H, 5.80; molecular weight, 2240 (calcd. for $(C_{22}H_{16})_8$: 94.28, 5.72, 2240). The polymer was soluble in benzene, xylene, chloroform, carbon tetrachloride; insoluble in alcohol, ether and acetic acid. It was separated into fractions by the addition of successive quantities of alcohol to a solution of 15 g. of the polymer in 800 cc. of benzene, the total weight of the five fractions collected being 14.5 g. The properties of the fractions are shown in the following table.

TABLE IV

PROPERTIES OF THE FRACTIONS

Fraction	M. p., °C.	Molecular weight (Rast's method in camphor)	Approx. no. of monomeric mols. per av. mol. of polymer	Viscosity. time of flow of 1% soln. in benzene[a]
1	365–368	3275	12	90.7 secs.
2	336–338	2485	9	86.4
3	317–319	1897	7	82.3
4	302–305	1380	5	81.0
5	286–290	1034	4	78.0

[a] Time of flow of (a) benzene, 67.0 secs.; (b) 1% solution of nnpolymerized cinnamal fluorene, 69.4 secs.

Antimony pentachloride was selected as the most active agent for the purpose of bringing about the catalytic polymerization of cinnamal fluorene after a survey had been made of the effect of a large number of reagents on cinnamal fluorene in chloroform solution. Other polymerization agents less effective than antimony pentachloride were: BCl_3,[13] $TiCl_4$, $SnCl_4$,[14] WCl_6, $MoCl_5$, $FeBr_3$, halides of aluminum, Na, K, CrO_2Cl_2, $SeOCl_2$. A slight action was exerted by P_2O_5 and $FeCl_3$. Of substances lacking in polymerizing action may be mentioned: H_2SO_4, $SbCl_3$, $AsCl_3$, $SiCl_4$, Na_2O_2, BaO_2, benzoyl peroxide, $TiCl_3$, BBr_3, $SnCl_2$, SnI_4, chlorides of Hg, Cu, Cd, Pb, Bi, Zn, Ni, Co.

Cinnamal Indene

This compound was prepared by the following procedure, which gave better yields and was more expeditious than the procedure originally described by Thiele.[15] To a solution of 10.4 g. of cinnamic aldehyde and 14.4 g. of pure indene in 40 cc. of methyl alcohol, 8.5 cc. of a 30% solution of potassium hydroxide in methyl alcohol was added and, after the solution had stood for fifteen minutes, the separated reddish crystals, consisting of cinnamal indene and hydroxycinnamyl cinnamal indene, were filtered off. By recrystallization from ethyl acetate, cinnamal indene (9 g.) was obtained as reddish-yellow needles melting at 190°. The mother liquor was evaporated and the residue taken up in 150 cc. of hot benzene. On cooling, fine yellow needles of hydroxycinnamyl cinnamal indene came out, the more soluble reddish cinnamal indene remaining in the mother liquor. The product was purified by recrystallization from hot benzene; m. p., 160–161°.

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[13] This gave a polymer melting at 195–196°.

[14] This was used (in the case of anethole) by Gerhardt as far back as 1845 (*J. prakt. Chem.*, 36 (I), 270).

[15] Thiele, Ber., 33, 3398 (1900).

Thermo-polymerization.—Cinnamal indene was heated in a sealed tube at 200° for three days. The red, brittle resin thus obtained was dissolved in benzene and precipitated with alcohol. (Unpolymerized cinnamal indene is not thrown out by alcohol from benzene.) After drying *in vacuo,* the polymeric product thus obtained consisted of a dark yellow powder; m. p. 266–268°; mol. wt., 1692; C, 93.80; H, 6.08 (calcd for $(C_{18}H_{14})_7$: 1610, 93.91, 6.09). The material was separated into four fractions by precipitation with absolute alcohol from benzene solution. The fractions gave the following results.

TABLE V

FRACTIONATION OF POLYCINNAMAL INDENE

Fraction	1	2	3	4
M. p., °C.	273–275	266–268	260–262	245–246
Mol. wt.	1892	1698	1534	1123

Polymerization by **Stannic Chloride.**—$SbCl_5$ was found to react with cinnamal indene so vigorously that it was difficult to avoid charring; hence $SnCl_4$, the action of which was not so vigorous, was used as a polymerization catalyst. To a solution of 4.5 g. of cinnamal indene in 75 cc. of chloroform was added 1.5 cc. of a 20% solution of $SnCl_4$ in chloroform and after the solution, which became dark red, had stood for two hours it was poured into 100 cc. of absolute alcohol. The precipitated polymer was purified by solution three times in chloroform followed by precipitation with alcohol; yield, 4.2 g. of a dark yellow powder; m. p. 238–242°; mol. wt., 972 (calcd. for $(C_{18}H_{14})_4$: 920).

Benzal Indene

Thermo-polymerization.—Benzal indene was heated at 178° in a sealed tube for five days. The red resin thus obtained was, unlike unpolymerized benzal indene, insoluble in alcohol. After purification by the precipitation of its (red) solution in xylene with alcohol, it was obtained as an orange-colored powder, m. p. 238–242°; mol. wt., 789; C, 93.95; H, 5.80 (calcd. for $(C_{16}H_{12})_4$: 816, 94.12, 5.88.).

Polymerization by Antimony **Pentachloride.**—To a solution of 3 g. of benzal indene in 60 cc. of chloroform was added 0.75 cc. of a 20% solution of $SbCl_5$ in chloroform and, after standing for half an hour, the deep blue solution was poured into 100 cc. of absolute alcohol. The precipitated polymer was purified by solution several times in benzene and precipitation with alcohol and was dried in *vacuo;* yield, 2.6 g. of a yellow powder; m. p., 252–255°; mol. wt. 1174 (calcd. for $(C_{16}H_{12})_6$: 1224).

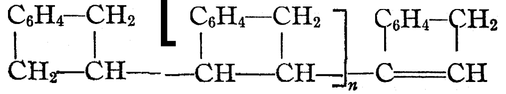
Hydroxybenzyl Benzal Indene

This compound was prepared by the following modification of the procedure described by Thiele.[15] To a mixture of 9 g. of pure indene and 16.5 g. of benzaldehyde cooled in a bath at 10° was added, drop by drop and with constant stirring, a solution of 0.5 g. of sodium in 20 cc. alcohol. After standing for two hours, the product which had separated was filtered off and washed, first with a little alcohol and then with water; yield, 17 g.; m. p. (from alcohol) 135–136°. From the mother liquor were obtained 1.5 g. of benzal indene (m. p., 88–89°) and a mixture of the two compounds melting at 120°. Polymerization was brought about by the addition of $SbCl_5$ to a chloroform solution, as in previous cases. After purification by precipitation three times by alcohol from a chloroform solution, the polymer was obtained in 95% yield as a deep yellow powder; m. p. 297–300°; mol. wt., 1928 (calcd. for $(C_{23}H_{18}O)_6$: 1860). The material gave red, non-colloidal solutions in most organic solvents but was insoluble in alcohol and in ether. $SnCl_4$ polymerized hydroxybenzyl benzal indene more slowly than did $SbCl_5$ and gave a lower polymeric product (m. p. 195–200°).

Summary

Indene is converted into high polymers by the catalytic action of antimony pentachloride and stannic chloride. The products are heterogeneous. The highest polymer isolated was represented by a fraction with a molecular weight corresponding to $(C_9H_8)_{29}$. The polymeric products obtained by heating indene are lower, the higher the temperature used. These products, too, are heterogeneous. There is a clear relationship between the melting point and molecular weight of polymers of indene.

All of the polyindenes, no matter what their molecular weight, contain one double bond per molecule. It is concluded that the polymerization of indene proceeds step-wise by the addition, involving the wandering of hydrogen, of successive molecules of the monomer, leading to products of the formula



$$\begin{array}{c} C_6H_4-CH_2 \\ | \qquad\quad | \\ CH_2-CH- \end{array}\left[\begin{array}{c} C_6H_4-CH_2 \\ | \qquad\quad | \\ -CH-CH- \end{array}\right]_n\begin{array}{c} C_6H_4-CH_2 \\ | \qquad\quad | \\ -C=CH \end{array}$$

Cinnamal fluorene yields high polymers when treated with antimony pentachloride or stannic chloride, the products being mixtures. Heating at 240–250° also causes it to polymerize. Cinnamal indene and benzal indene also can be polymerized by heat and by catalysts. Hydroxybenzyl benzal indene can be polymerized by antimony pentachloride.

Montreal, Canada

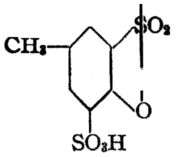
[Contribution from the Chemistry Laboratory of the University of Michigan]

THE PREPARATION OF THE SULFONYLIDES OF CRESOL- AND CHLOROPHENOL DISULFONIC ACIDS

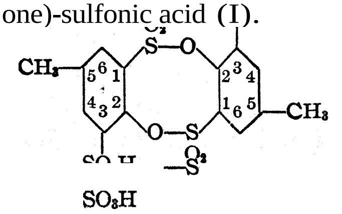
By C. S. Schoepfle, F. J. Van Natta and R. G. Clarkson

Received November 25, 1927 Published April 5, 1928

Raschig[1] found that p-cresol disulfonic acid was dehydrated by treatment with fuming sulfuric acid to give a product which was supposedly the monomolecular (p-cresol sulfone)-sulfonic acid (I).



(I)



(II)

In a very brief description of this compound, the fact was mentioned that it gave insoluble sodium and potassium salts which might be of value in analytical chemistry. Later,[2] Raschig concluded that his product was a disulfonic acid of *p*-methylphenylene-*o*-sulfonylide or, as it will

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[1] Raschig, *Z. angew. Chem.*, 25, 1944 (1912); *Chem. Zeit.*, 36, 1070 (1912).

[2] See Anschütz, Ann., 415, 65 (1918).

be named in this paper, (2-hydroxy-5-methyl-*m*-benzene disulfonic acid) sulfonylide (II). Examples of this class had been prepared previously by Schiff[3] and by Anschütz.[4] In order to establish the structure of this compound, Anschutz[2] prepared the corresponding sulfonyl chloride and found that its molecular weight in nitrobenzene agreed with the bimolecular sulfonylide formula.

The purpose of the present investigation was (1) to determine if the formation of sulfonylides is a general reaction for substituted phenols upon treatment with fuming sulfuric acid, (2) to obtain further proof of the bimolecular structure of these compounds and **(3)** to determine the solubility of the sodium salts.

It has been found that the sulfonylide described by Raschig can be prepared in 87% yield by heating p-cresol for several hours at 100° with fifteen times its weight of fuming sulfuric acid containing 20% of sulfur trioxide. Under similar conditions, sulfonylides were obtained from o-cresol, o-chlorophenol and p-chlorophenol in 80–85% yields, and from *m*-chlorophenol in 50% yield; no sulfonylide was obtained from m-cresol.

The corresponding sulfonyl chlorides, sulfonamides and the methyl esters of the sulfonylides of p-cresol disulfonic acid and of o-cresol disulfonic acid were prepared and attempts to determine their molecular weights were made. The molecular weights of the sulfonyl chlorides could not be obtained for, although they were soluble in boiling nitrobenzene, the solutions gradually darkened in color and in a short time became black, indicating decomposition. The sulfonamides were not sufficiently soluble to permit molecular weight determinations, but the esters proved to be more suitable. The methyl esters of the sulfonylides of *p*-cresol disulfonic acid and of o-cresol disulfonic acid both gave molecular weights in methyl alcohol which indicated a monomolecular structure. However, the molecular weight of the sulfonylide of o-cresol disulfonic acid in acetone and in acetic acid agreed with the bimolecular formula and the same was true of the corresponding methyl ester in acetone and in ethyl acetate. It appeared, therefore, as if the molecular weights of the esters in methyl alcohol were abnormal and in order to confirm this the dimethyl ester of p-cresol disulfonic acid was prepared and its molecular weight determined in methyl alcohol, acetone and ethyl acetate. The results showed that acetone and ethyl acetate gave the correct value but that the molecular weight in methyl alcohol was again abnormally low. The molecular weights were determined by the Menzies method[5] except in the case of acetic acid where the Beckmann ebullioscopic method was used.

[3] **Schiff,** *Ann.,* **178, 187 (1875).**

[4] **Anschütz,** ***Ber.,*** **45, 2378 (1912).**

[5] **Menzies and Wright, THIS JOURNAL, 43, 2314 (1921).**

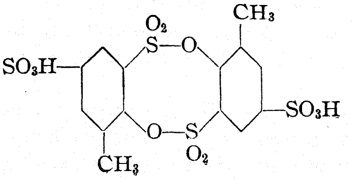
Rough solubility determinations were made for the sodium salts of the sulfonylides. The solubility of the sodium salt of the sulfonylide of *p*-chlorophenol disulfonic acid was found to be 1.6 g. per 100 g. of water at 25°, while the others varied in solubility from 0.6 g. to 0.0 g. per 100 g. of water. A mono-sulfonic acid of (6-hydroxy-*m*-toluene sulfonic acid) sulfonylide was prepared and its sodium salt proved to be soluble only to the extent of 0.13 g. per 100 g. of water at 25°. The alkali salts of the acids described in this paper are being investigated in this Laboratory by Dr. H. H. Willard in regard to their possible value in analytical chemistry.

Experimental Part

(2-Hydroxy-5-methyl-*m*-benzene Disulfonic Acid) Sulfonylide (II) has been described by Raschig,[1] who gave no details of the method of preparation, and also by Anschütz,[2] who heated *p*-cresol disulfonic acid at 100° with twice its weight of fuming sulfuric acid containing 60% of sulfur trioxide. In neither case was the yield stated. This sulfonylide and also the other sulfonylides described in this paper were obtained in good yields by treating the cresol or the chlorophenol with ten to fifteen times its weight of fuming sulfuric acid containing 20% of sulfur trioxide. Since the reaction is rather vigorous in its initial stage, the following general procedure was adopted.

Fifteen g. of 95% sulfuric acid was added to 10 g. of the cresol or chlorophenol and the solution heated on the steam-bath for a few minutes, after which it was cooled and treated with 135 g. of fuming sulfuric acid containing 25% of sulfur trioxide. The flask was then immersed in a steam-bath and heated for two to eight hours, during which time the sulfonylide usually crystallized. The crystals were very fine and difficult to filter; therefore the mixture was poured over ice, diluted with water and heated to about 100° when a clear solution was obtained—volumes ranging from 350 cc. to 700 cc. were required. When the solution cooled, the sulfonylide crystallized in colorless needles or in plates which were filtered, washed with 20% hydrochloric acid and dried in air. The water of crystallization was determined by drying the sample for twelve to twenty hours at temperatures varying from 120 to 145° depending upon the stability of the compound; however, in the case of (5-chloro-2-hydroxy-*m*-benzene disulfonic acid) sulfonylide, which could not be dried above 135° because of slight decomposition, a period of eighty hours was required before constant weight was obtained. All of the sulfonylides decompose above 300° without melting. They are soluble in water and in alcohol, soluble in some cases in acetone and in acetic acid, and insoluble in the other common organic solvents and in inorganic acids. They are all readily recrystallized from dilute hydrochloric acid.

The following structures have been assigned to the sulfonylides on the basis that a hydroxyl group has a greater directing influence than a methyl group or a chlorine atom. The yields, the number of molecules of water of crystallization, the analyses and the crystalline forms of the sulfonylides are given in Table I.



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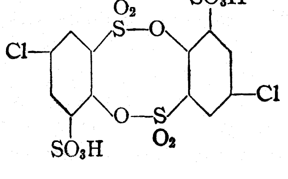

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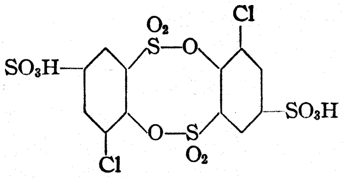

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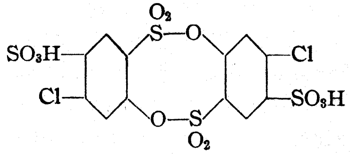

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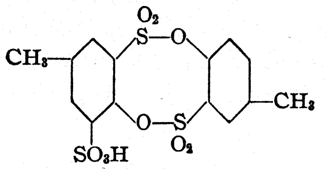

(VII)

TABLE I

DATA ON AND ANALYSES OF SULFONYLIDE DERIVATIVES OF *m*-BENZENE DISULFONIC ACID

Derivative	Time of heating, hours	Yield, %	Water of crystn., moles	Cryst. form	Sulfur, % Calcd.	Sulfur, % Found	Replaceable H,[a] % Calcd.	Replaceable H,[a] % Found	Water of crystn., % Calcd.	Water of crystn., % Found
2-Hydroxy-5-methyl (II)	2	87	4[b]	Needles	22.41	22.15	0.352	0.345	12.59	12.62
4-Hydroxy-5-methyl (III)[c,d]	6	80	6	Elon. plates	21.08	20.72	.331	.333	17.76	17.71
5-Chloro-2-hydroxy (IV)	6	84	4	Elon. plates	20.91	20.84	.329	.329	11.75	11.76
5-Chloro-4-hydroxy (V)	6	83	6	Plates	19.75	19.50	...	[e]	16.65	16.58
6-Chloro-4-hydroxy (VI)[f]	8	49	8	Plates	18.71	18.55	.294	.302	21.03	20.81

[a] By titration with standard sodium hydroxide solution.

[b] Anschütz found three molecules of water of crystallization.

[c] Molecular weight in acetone (K = 17.2): 505, 528; in acetic acid (K = 30.7): 495, 485. Calcd. for $C_{14}H_{12}O_{12}S_4$: 500.4.

[d] This sulfonylide has been prepared by Pollak and Gebauer-Fülnegg (ref. 8) by treating o-cresol with chlorosulfonic acid and is described by them as an amorphous powder which could not be obtained in crystalline state. Since the sulfonylide crystallizes beautifully from dilute inorganic acids, their product could not have been pure.

[e] Results were high due to partial hydrolysis of the sulfonylide upon titration.

[f] This compound was prepared by heating m-chlorophenol with 15 times its weight of fuming sulfuric acid containing 25% of sulfur trioxide.

Disulfonamide of (2-Hydroxy-5-methyl-m-benzene Disulfonic Acid) Sulfonylide.—The corresponding disulfonyl chloride[7] was obtained in quantitative yield by heating the sulfonylide with phosphorus pentachloride for one hour at 130°, adding enough phosphorus oxychloride to keep the mixture fluid. The compound was purified by recrystallization from benzene with a Soxhlet extractor. It was soluble in hot nitrobenzene but decomposed slowly in boiling nitrobenzene so that its molecular weight could not be obtained.

Ten g. of the crude, dry disulfonyl chloride was suspended in 150 cc. of nitrobenzene, the flask immersed in an oil-bath at 175–180° and a vigorous stream of dry ammonia passed into the mixture for one hour. The precipitate was filtered, washed with alcohol and then washed thoroughly with water to remove the ammonium chloride; yield, 8.5 g. (92%). The disulfonamide is insoluble in water and the common organic solvents, but can be recrystallized from acetone or acetic acid by means of a Soxhlet extractor. Very fine, colorless needles were obtained which decompose above 300° without melting.

Anal. Calcd. for $C_{14}H_{14}O_{10}S_4N_2$: S, 25.73; N, 5.62. Found: S, 25.44; N (Kjeldahl), 5.58.

Diethyl Ester of (**2-Hydroxy-5-methyl-*m*-benzene Disulfonic** Acid) **Sulfonylide.**—Ten g. of the anhydrous silver salt of the sulfonylide was suspended in 125 cc. of absolute ethyl alcohol, 10 g. of ethyl iodide added and the mixture refluxed on the steam-bath for several hours. The precipitated silver iodide was filtered and the solution poured slowly into absolute ether, whereby the ester was obtained in fine, colorless, elongated plates; yield, 7.6 g. (97%). It is soluble in ethyl alcohol and in hot methyl alcohol, but insoluble in ether, benzene, acetone, ethyl acetate, chloroform and acetic acid. The ester is rapidly hydrolyzed in water even at room temperature; consequently titration with standard alkali affords the most convenient method of analysis.

Anal. 0.7216 g. required 25.16 cc. of $N/10$ NaOH. Calcd. for $C_{18}H_{20}O_{12}S_4$: 25.94 cc. S, calcd.: 23.05. Found: 22.32.

Both analyses gave values about 3% low, due probably to a small amount of alcohol either occluded in the crystals or held as alcohol of crystallization. Drying in vacuum did not remove this alcohol, and heating to 90° caused decomposition into the corresponding sulfonylide and ethylene.[6] The ester when recrystallized from methyl alcohol contained two molecules of methyl alcohol of crystallization.

Dimethyl Ester.—The **dimethyl** ester was prepared in 95% yield by treating the anhydrous silver salt with methyl iodide, following the procedure described for the preparation of the ethyl ester. The absolute methyl alcohol which was used as the solvent was prepared by dissolving magnesium in the alcohol and distilling from the magnesium methylate which was formed.[7] The ester was obtained in fine, colorless crystals by pouring the methyl alcohol solution into ether, or by concentrating the solution. The crystals contain two molecules of methyl alcohol of crystallization which is given off readily at a temperature of 90°. It chars without melting when heated above 250°. The ester is soluble in methyl and ethyl alcohol, and insoluble in the other common organic solvents.

Anal. 0.3770 g. required 14.25 cc. of $N/10$ NaOH. Calcd. for $C_{16}H_{16}O_{12}S_4$: 14.27 cc. S, calcd.: 24.27. Found: 23.97. Molecular weight in methyl alcohol ($K = 8.8$): 271, 295. Calcd.: 528.4.

Disulfonamide of (**4-Hydroxy-5-methylm-benzene Disulfonic** Acid) **Sulfonylide.**—The disulfonyl chloride of this sulfonylide has been described by Pollak and Gebauer-Fülnegg,[8] who prepared it by treating o-cresol with chlorosulfonic acid. We obtained the compound in quantitative yield by heating the sulfonylide with phosphorus pentachloride, using phosphorus oxychloride as the solvent. Ten g. of the crude, dry disulfonyl chloride was suspended in 150 cc. of nitrobenzene and dry ammonia passed into the mixture for one hour at a temperature of 100°. The precipitate was filtered, washed with alcohol and then washed thoroughly with water. The disulfonamide was recrystallized from acetic acid using a Soxhlet extractor and was obtained in small, colorless crystals which decompose above 300° without melting; yield, 8.8 g. (95%). The compound is slightly soluble in hot acetic acid and in acetone, and is insoluble in the other common organic solvents.

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[6] Foldi, *Ber.*, 60B, 656 (1927).

[7] Bjerrum and Zechmeister, Ber., ***56,*** 894 (1923).

[8] Pollak and Gebauer-Fülnegg, *Monatsh.*, 46, 387 (1925).

Anal. Calcd. for $C_{14}H_{14}O_{10}S_4N_2$: S, 25.73; N, 5.62. Found: S, 25.51: N **(Kjeldahl),** 5.59.

Dimethyl Ester of **(4-Hydroxy-5-methyl-712-benzene** Disulfonic Acid) **Sulfonylide.**—Ten g. of the anhydrous silver salt of the sulfonylide and 7.5 g. of methyl iodide in absolute methyl alcohol were heated for one hour on the steam-bath. The precipitated silver iodide was filtered, the solution concentrated under reduced pressure and the residue dissolved in hot ethyl acetate. Upon cooling, the ester was obtained in colorless crystals containing two molecules of methyl alcohol of crystallization; yield, 7.6 g. (92). The alcohol of crystallization is given off slowly at a temperature of 60°; drying at temperatures above 90° usually results in decomposition. The compound chars above 250° without melting. It is soluble in methyl and ethyl alcohol and in acetone, slightly soluble in ethyl acetate and insoluble in ether, benzene and carbon tetrachloride.

Anal. 0.4562 g. required 17.26 cc. of $N/10$ NaOH. Calcd. for $C_{16}H_{16}O_{12}S_4$: 17.27 cc. S, calcd.: 24.27. Found: 23.87. Molecular weight in methyl alcohol: 261,278; in acetone: 507,517; in ethyl acetate ($K = 27.9$): 495,530. Calcd.: 528.4.

(6-Hydroxy-m-toluene **Sulfonic** Acid) **Sulfonylide-5-sulfonic** Acid **(VII).**—(6-Mydroxy-m-toluene sulfonic acid) sulfonylide was prepared by the action of phosphorus oxychloride on p-cresol sulfonic acid as described by **Anschütz.**[2] It was found that the crude sulfonic acid obtained from the sulfonation of p-cresol could be used without further purification. Fifty g. of *p*-cresol was treated with an equal weight of 100% sulfuric acid and the mixture heated for one hour on the steam-bath. The sulfonic acid which crystallized when the solution cooled was sucked as dry as possible on a porous glass filter and then heated for six hours on the steam-bath with twice its weight of phosphorus oxychloride. The mixture was cooled and decomposed with ice, whereupon the sulfonylide was obtained as a sticky mass which hardened to a solid. The lumps were boiled in acetic acid, from which the sulfonylide was recovered in small, colorless crystals; yield, 20 g. (25%).

Five g. of the sulfonylide was treated with 50 g. of fuming sulfuric acid containing 25% of sulfur trioxide and the mixture allowed to stand at room temperature until a clear solution was obtained. It was then poured over ice and the sulfonic acid which was precipitated was sucked as dry as possible on a funnel and recrystallized from acetic acid. Colorless, elongated plates were obtained which melted at 220–222°, depending upon the rate of heating. The air-dried crystals contain approximately two molecules of water of crystallization; yield, 4.3 g. (64%). The compound is soluble in alcohol and in hot acetic acid, slightly soluble in hot water and in hot acetone, and insoluble in ether, benzene, ethyl acetate, carbon disulfide and carbon tetrachloride. This acid presents a rather unusual phenomenon in that a solution in hot water sets to a gel on cooling. Titration with standard alkali gave high results, due to hydrolysis of the sulfonylide; the results with sodium carbonate solution were somewhat better but were not entirely satisfactory.

Anal. Calcd. for $C_{14}H_{12}O_9S_3.2H_2O$: S, 21.08; H_2O, 7.90. Found: S, 20.74; H_2O, 7.75 (loss in weight on drying for four hours at 145°). Molecular weight in acetic acid: 363. Calcd. for $C_{14}H_{12}O_9S_3$: 420.3.

Methyl Ester of (6-Hydroxy-m-toluene Sulfonic Acid) Sulfonylide-5-sulfonic Acid.—Ten g. of the anhydrous silver salt and 5 g. of methyl iodide in 300 cc. of absolute methyl alcohol were heated on the steam-bath for several hours. The precipitated silver iodide was filtered and the solution allowed to cool, whereupon colorless crystals of the ester were obtained. The crystals contained about one and one-half molecules of methyl alcohol of crystallization, which was given off upon drying at 90°; yield, 7.2 g. (87%). When heated to higher temperatures, the ester decomposed without charring to give the sulfonic acid, which then melted at about 220°. The compound is soluble in ethyl alcohol, fairly soluble in hot methyl alcohol, slightly soluble in hot acetone and insoluble in ether, benzene, ethyl acetate, carbon disulfide and carbon tetrachloride.

Anal. Calcd. for $C_{15}H_{14}O_9S_3$: S, 22.15. Found: 22.09. Molecular weight in ethyl alcohol (K = 11.7): 412. Calcd.: 434.3.

Dimethyl Ester of 2-Hydroxy-5-methyl-m-benzene Disulfonic Acid.—Ten g. of the anhydrous silver salt of 2-hydroxy-5-methyl-*m*-benzene disulfonic acid[9] and 8 *g.* of methyl iodide were added to about 75 cc. of absolute methyl alcohol in a stoppered flask and allowed to stand for several hours with occasional shaking. The precipitated silver iodide was filtered, the alcohol distilled off as completely as possible under reduced pressure at 50–60°, and the residue dissolved in a small amount of hot methyl benzoate. Upon cooling, the ester was obtained in small, colorless crystals which were filtered and washed with methyl benzoate and benzene. A further crop of crystals was obtained by adding benzene to the filtrate. The crystals contained methyl alcohol of crystallization which was given off upon drying at 80°; yield, 5.3 g. (86%); m. p. 148–149°. The ester is soluble in alcohol and acetone, slightly soluble in ether and in ethyl acetate and insoluble in benzene, petroleum ether, carbon disulfide and carbon tetrachloride.

Anal. 0.2009 *g.* required 13.28 cc. of $N/10$ NaOH. Calcd. for $C_9H_{12}O_7S_2$: 13.56 cc. S, calcd.: 21.65. Found: 21.41. Molecular weight in methyl alcohol: 190, 192; in acetone: 297, 305; in ethyl acetate: 295, 305. Calcd.: 296.2.

Solubility of the Sodium Salts.—A solution of the recrystallized sodium salt was prepared of sufficient concentration so that, upon cooling, part of the salt would crystallize. The flask was placed in a thermostat at a temperature of 25° for forty-eight hours or longer, after which about 50 cc. of the solution was filtered into a weighed, glass-stoppered Erlenmeyer flask and the exact weight determined. The water was evaporated at about 80° and the residue dried to constant weight at a temperature of 120° to remove water of crystallization. Considerable difficulty was experienced in obtaining satisfactory checks, due possibly to the formation of different hydrates; the values given in Table II represent the average of several determinations in each case and express the order of magnitude of the solubilities.

TABLE II

SOLUBILITIES OF SODIUM SALTS OF SULFONYLIDE DERIVATIVES OF *m*-BENZENE DISULFONIC ACID

Sodium salt of	Soly., g. per 100 g. of water	Sodium salt of	Soly., g. per 100 g. of water
2-Hydroxy-5-methyl-[a]	0.75	5-Chloro-4-hydroxy-	0.58
4-Hydroxy-5-methyl-	0.61	6-Chloro-4-hydroxy-	0.89
5-Chloro-2-hydroxy-	1.6	(6-Hydroxy-m-toluene sulfonic acid) sulfonylide-5-sulfonic acid	.13

[a] Dried at 140°.

Summary

1. A satisfactory method has been described for the preparation in good yields of sulfonylides of the disulfonic acids of *p*-cresol, o-cresol, *p*-chlorophenol, o-chlorophenol and *m*-chlorophenol. A monosulfonic acid of (6-hydroxy-*m*-toluene sulfonic acid) sulfonylide has **also** been prepared and described.

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[9] Anschütz and Cürten, *Ann.*, 457, 264 (1927).

2. The sulfonamides and the methyl esters of the sulfonylides of p-cresol disulfonic acid and of o-cresol disulfonic acid have been prepared. The molecular weights of the esters have furnished further proof of the bimolecular formula which has been assigned to the sulfonylides.

3. The approximate solubility of the sodium salt of each of the sulfonylides has been determined.

ANN ARBOR, MICHIGAN

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

THE ACTION OF CYCLOHEXYLMAGNESIUM BROMIDE ON DERIVATIVES OF OXALIC ACID

BY CHESTER G. GAUERKE[1] WITH C. S. MARVEL

RECEIVED DECEMBER 6, 1927 PUBLISHED APRIL 5, 1928

The reactions of various Grignard reagents on esters of oxalic acid have been studied by many different chemists. Valeur,[2] Bouvet[3] and Meerwein[4] have reported varying yields of tetra-alkyl ethylene glycols and of ethyl dialkyglycolates from the action of Grignard reagents on ethyl oxalate. Egorowa[5] and Wenus[6] have found that tertiary alkyl magnesium halides react with ethyl oxalate to give esters of the general formula, $R_3CCHOHCO_2C_2H_5$. Hepworth[7] has observed that by limiting the amount of the alkyl Grignard reagent used, the reaction can be confined to one of the ester groups and thus good yields of disubstituted glycolic esters can be obtained. On the other hand, Valeur[8] has observed that phenylmagnesium bromide reacts with methyl oxalate to give benzopinacol, $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$, in very good yields.

In attempting to find a satisfactory method for the preparation of tetracyclohexyl ethylene glycol, $(C_6H_{11})_2C(OH)C(OH)(C_6H_{11})_2$, the reaction of cyclohexylmagnesium bromide and ethyl oxalate was studied. It was found that the main product of this reaction was ethyl dicyclohexylgycolate, $(C_6H_{11})_2C(OH)CO_2C_2H_5$. Only small amounts of the desired glycol were obtained even when a large excess of the Grignard reagent was used. By replacing ether, which is the common solvent for the Grignard

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[1] This communication is an abstract of a thesis submitted by Chester G. Gauerke in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Valeur, *Compt. rend.*, 132,833 (1901).

[3] Bouvet, *Bull, soc. chim.*, [4] 17,202 (footnote) (1915).

[4] Meerwein, *Ann.*, 419, 151 (1919).

[5] Egorowa, J. *Russ. Phys.-Chem. Soc.*, 41, 1454 (1909); *Chem. Zent.*, [I] *81*, 1003 (1910).

[6] Wenus, *J. Russ. Phys.-Chem. Soc.*, 46, 1332 (1914); *Chem. Zent.*, [I] *86*, 1055 (1915).

[7] Hepworth, *J. Chem. Soc.*, 115, 1203 (1919).

[8] Valeur, Bull. *soc. chim.*, *[3] 29, 684* (1903).

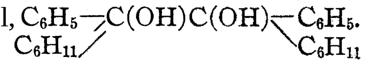
reaction, by benzene the yield of glycol was increased slightly. However, the reaction runs too poorly to be of use as a source for this compound. Two other esters of oxalic acid, namely methyl and *iso*propyl, were used in place of the ethyl ester, but the main products of the reactions were respectively the methyl and the isopropyl esters of dicyclohexylglycolic acid.

Oxalyl chloride was next used since it was expected that this would prove more reactive. This did yield traces of the desired glycol but the main reaction product was dicylohexyl ketone. This indicates that decomposition of oxalyl chloride or of some intermediate product must occur.

The failure of cyclohexylmagnesium bromide to produce the glycol in good yields, when the corresponding phenyl derivative works very well, is of considerable interest. It would be expected that the saturated ring would occupy a somewhat greater space and that steric hindrance effects would be more noticeable in cyclohexyl derivatives than in the corresponding phenyl compounds. However, it would hardly be expected that the difference in size between the saturated and the phenyl rings would be sufficient to stop the reaction at the hydroxy ester stage when the saturated ring is used.

If the reaction proceeds in the same stages when phenylmagnesium bromide reacts with an oxalate, an intermediate product would be an ester of benzilic acid, $(C_6H_5)_2C(OH)CO_2H$. It was thought that further information concerning the reactions could be obtained by studying the effects of various Grignard reagents on the esters of dicyclohexylglycolic acid and of benzilic acid.

It was found that ethyl dicyclohexylglycolate was recovered unchanged after prolonged action of cyclohexylmagnesium bromide, phenylmagnesium bromide or ethylmagnesium bromide. On the other hand, methyl benzilate reacts with an excess of cyclohexylmagnesium bromide to give a hydroxyketone, $(C_6H_5)_2C(OH)COC_6H_{11}$. The reaction apparently stops at this stage since none of the glycol could be obtained. With benzil, $C_6H_5COCOC_6H_5$, cyclohexylmagnesium bromide produces the glycol,



$$\underset{C_6H_{11}\diagup}{C_6H_5\diagdown}C(OH)C(OH)\underset{\diagdown C_6H_{11}}{\diagup C_6H_5}.$$

These observations are of interest in showing the marked difference in the behavior of the phenyl and cyclohexyl groups in these reactions. However, they are not of such a nature as to allow one to conclude whether the difference in the reactions is due to steric hindrance effects or to some activating influence of the phenyl groups on neighboring carbonyl groups.

In further attempting to obtain tetracyclohexyl ethylene glycol the reduction of dicyclohexyl ketone was studied. No greater success resulted with this reaction.

Experimental Part

Cyclohexylmagnesium Bromide and Ethyl **Oxalate.**—In a 2-liter, three-necked flask fitted with a stirrer, a reflux condenser and separatory funnel was placed 1.2 moles of cyclohexylmagnesium bromide (2 N solution in ether) and to it was added a solution of 32 g. (0.22 mole) of ethyl oxalate in 100 cc. of dry benzene during a period of two hours. When this addition was complete 1 liter of dry benzene was added and most of the ether was removed from the reaction mixture by distillation. The mixture was then stirred continuously and heated to gentle boiling for about four days until a test[9] for the Grignard reagent was negative. The reaction mixture was decomposed with dilute sulfuric acid in the usual way and the solvent was removed by distillation at ordinary pressure. The residue was distilled under reduced pressure and two main fractions were obtained.

The first of these boiled at 138–150° at 4 mm. and weighed 14 g. On standing it partially solidified and on crystallization from acetone yielded a white, crystalline solid, m. p. 69° (corr.). Analysis showed that this was ethyl dicyclohexylglycolate. This was also shown by hydrolysis and isolation of the acid.

Anal. Subs., 0.2004, 0.2028; CO_2, 0.5259, 0.5317; H_2O, 0.1866, 0.1887. Calcd. for $C_{16}H_{28}O_3$; C, 71.59; H, 10.52. Found: C, 71.59, 71.52; H, 10.42, 10.42.

Ten grams of the ester were boiled under reflux in a copper flask with an excess of 50% potassium hydroxide for about five days. On cooling and filtering the solution 4 g. of unchanged ester was recovered. On acidifying the solution dicyclohexyglycolic acid separated. It was purified by solution in alkali and reprecipitation. It melted at 171–172° (corr.) and gave a neutral equivalent of 239 instead of theoretical 240. The acid was decomposed by cold concd. sulfuric acid to give carbon monoxide, water and dicyclohexyl ketone. This was identified by converting to the oxime, m. p. 158–160°, which agrees with the melting point recorded in the literature.[10]

The second fraction obtained from the reaction of cyclohexylmagnesium bromide and ethyl oxalate boiled at 180–210° at 0.5–1 mm. pressure. It weighed 4–5 g. It solidified on standing and after recrystallization from acetone yielded about 0.5 g. of a white, crystalline solid, m. p. 151–152" (corr.). It analyzed correctly for tetracyclohexyl ethylene glycol.

Anal. Subs., 0.1000, 0.1007; CO_2, 0.2893, 0.2934; H_2O, 0.1069, 0.1057. Calcd. for $C_{26}H_{46}O_2$: C, 79.93; H, 11.87. Found: C, 78.93, 79.49; H, 11.96, 11.74.

The reaction of cyclohexylmagnesium bromide and ethyl oxalate in anhydrous ether was studied under a variety of conditions as to concentration of reacting substances and time of reaction without giving the desired glycol. Some dicyclohexyl was isolated. The yield of pure ethyl dicyclohexylglycolate was never greater than about 20% of the theoretical amount.

Cyclohexylmagnesium Bromide and Other Esters of **Oxalic** Acid.—One mole of cyclohexylmagnesium bromide and 25 g. (0.21 mole) of methyl oxalate in ether solution gave 14 g. of a product boiling at 135–160° at 4–5 mm. From this after two crystallizations from acetone 6 g. of pure methyl dicyclohexylglycolate, m. p. 48.5' (corr.), was obtained.

Anal. Subs., 0.1071; CO_2, 0.2766; H_2O, 0.0992. Calcd. for $C_{15}H_{26}O_3$: C, 70.81; H, 10.30. Found: C, 70.46; H, 10.36.

In a similar way 1.01 moles of cyelohexylmagnesium bromide and 30 g. (0.172 mole) of isopropyl oxalate gave 8.5 g. of a product boiling at 140–160° at 7 mm., from

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[9] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925).

[10] Zelinsky and Gawerdowskaja, *Ber.*, 60,714 (1927).

which after two crystallizations from acetone 4 g. of pure *iso*propyl dicyclohexylglycolate, m. p. 80° (corr.), was obtained.

Anal. Subs., 0.1325; CO_2, 0.3526, H_2O, 0.1260. Calcd. for $C_{17}H_{30}O_3$; C, 72.29; H, 10.71. Found: C, 72 60; H, 10.64.

Grignard Reagents and Ethyl **Dicyclohexylglycolate.**—Three solutions of ethyl dicyclohexylglycolate in dry benzene were treated with ether solutions of excess cyclohexylmagnesium bromide, phenylmagnesium bromide and ethylmagnesium bromide, respectively. The solutions were refluxed for long periods, but on working up the mixtures about 90% of the ester was recovered unchanged in each case.

Cyclohexylmagnesium Bromide and Methyl **Benzilate.**—To 0 73 of a mole of cyclohexylmagnesium bromide in 300 cc. of di-n-butyl ether,[11] in a 2-liter flask fitted with stirrer, reflux condenser and separatory funnel, was added 50 g. (0.2 mole) of methyl benzilate in 200 cc. of dry ether. The reaction mixture was stirred and gently boiled for about twenty-four hours until the test for the Grignard reagent was negative. An additional 0.12 of a mole of the Grignard reagent was added and the heating and stirring were continued for two days until the test for the Grignard reagent was again negative. The reaction mixture was worked up in the usual way and most of the di-n-butyl ether was removed by distillation under reduced pressure. The residue (about 150 cc.) was cooled overnight at −10° and a solid separated. The solid was collected on a filter. From the mother liquors a second crop of crystals was obtained. The product was recrystallized from ligroin and 23 g. of pure crystals, m. p. 112.5° (corr.), was obtained. Analysis showed that this product was the hydroxy ketone, $(C_6H_5)_2C(OH)COC_6H_{11}$.

Anal. Subs., 0.1158, 0.1060; CO_2, 0.3468, 0.3171; H_2O, 0.0781, 0.0718. Calcd. for $C_{20}H_{22}O_2$: C, 81.59; H, 7.53. Found: C, 81.70, 81.61; H, 7.54, 7.57.

A sample of this product was boiled with alcoholic potassium hydroxide and was thus decomposed into the potassium salt of hexahydrobenzoic acid and diphenyl carbinol. Phenylbenzoin decomposes in a like manner to give potassium benzoate and diphenyl carbinol.[12]

When ethyl ether was used as the solvent, only small amounts of the hydroxy ketone were obtained.

Cyclohexylmagnesium Bromide and **Benzil.**—To 0.4 of a mole of cyclohexylmagnesium bromide in 215 cc. of ether was added 44 g. (0.21 mole) of benzil in 250 cc. of ether over a period of four hours. The reaction mixture was stirred at room temperature for about eight hours until the test for the Grignard reagent was negative. Then an additional 0.5 of a mole of the Grignard reagent was added and the solution was stirred and refluxed for about six hours. After decomposing the reaction mixture in the usual way, the ether layer was separated and evaporated. On standing a solid separated from the residue and the mixture was filtered with suction. The filtrate was steam distilled and another crop of crystals was filtered from the solution left behind. On recrystallizing the solid from ether 8 g. of a product, m. p. 150–151° (corr.), was obtained. Analysis showed that the product was the expected symmetrical diphenyl dicyclohexyl ethylene glycol.

Anal. Subs., 0.1375; CO_2, 0.4172, H_2O, 0.1124. Calcd. for $C_{26}H_{34}O_2$: C, 82.48; H, 9.06. Found: C, 82.78; H, 9.14.

Attempts to Prepare **Tetracyclohexyl** Ethylene Glycol by the Reduction **of Di**cyclohexyl Ketone.—Dicyclohexyl ketone was prepared from cyclohexylmagnesium bromide and hexahydrobenzoyl chloride according to the method of Johnson and Daw-

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[11] The use of di-n-butyl ether as a solvent for the Grignard reaction has been investigated in this Laboratory and will be discussed in detail in another paper.

[12] Nef, *Ann.*, 308, 291 (1899).

son.[13] When this ketone was treated with magnesium and iodine according to the method of Gomberg and Bachmann,[14] it was recovered unchanged. Magnesium amalgam in benzene followed by water did not cause reduction. Sodium and alcohol reduced the ketone to give a 76% yield of dicyclohexyl carbinol.

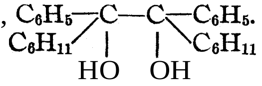
Summary

1. Cyclohexylmagnesium bromide reacts with esters of oxalic acid to give as the main product the corresponding ester of dicyclohexylglycolic acid. Small amounts of tetracyclohexyl ethylene glycol can be obtained.

2. Ethyl dicyclohexylglycolate does not react readily with either ethylmagnesium bromide, phenylmagnesium bromide or cyclohexylmagnesium bromide.

3. Methyl benzilate reacts with cyclohexylmagnesium bromide to give an hydroxy ketone, $(C_6H_5)_2C(OH)COC_6H_{11}$.

4. Benzil reacts with cyclohexylmagnesium bromide to give the symmetrical diphenyl dicyclohexyl ethylene glycol,



$C_6H_5-C(C_6H_{11})(OH)-C(OH)(C_6H_{11})-C_6H_5$.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. STEPHEN'S COLLEGE]

ORGANIC SELENIUM COMPOUNDS. SOME DERIVATIVES OF AROMATIC SELENO-ETHERS

BY DUNCAN GRAHAM FOSTER AND STANLEY F. BROWN

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Introductory

The researches reported in this paper originated in an attempt to duplicate, with compounds containing selenium, certain investigations conducted by Reid, with the senior author of this paper,[1] and with other investigators,[2,3] upon the influence of a sulfur atom in varying positions in the molecule on the color of a series of azo dyes. It had been our intention to employ exactly analogous methods to those outlined in references (1) and (2) in order to prepare nitro seleno-ethers, $O_2NC_6H_4SeR$, and from them amino seleno-ethers of the type, $H_2NC_6H_4SeR$, which could be diazotized and coupled with standard intermediates to give azo dyes.

These methods were found to be completely unfruitful because of the instability of the *o*- and *p*-nitroselenophenols, $O_2NC_6H_4SeH$, which oxidize

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[13] Private communication.

[14] Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927).

[1] Foster and Reid, THIS JOURNAL, 46, 1936 (1924).

[2] Waldron and Reid, *ibid.*, 45, 2399 (1923).

[3] Palmer and Reid, *ibid.*, 48, 528 (1926).

rapidly back to the diphenyl diselenides, $O_2NC_6H_4Se_2C_6H_4NO_2$, on coming in contact with the air like their sulfur analogs.[4,5]

We then tried to nitrate some seleno-ethers, C_6H_5SeR, with a nitrating mixture, by Gattermann's method, without results. Fuming nitric acid, however, did react with phenyl seleno-ethers, giving some crystallizable solids, but the reaction was found to be oxidation rather than nitration and no nitro group could be detected in the products. The oxidation products produced by this method seemed to be sufficiently interesting and sufficiently different from their sulfur analogs to warrant a special investigation, the results of which are set down in this paper.

Theoretical and Experimental

The most interesting differences between the aromatic seleno-ethers and the corresponding sulfur compounds are the increasingly basic properties of oxidized selenium, shown by the tendency to form loose molecular addition products, and the tendency of the former substances to exist in the hexavalent rather than in the tetravalent condition. Stoecker and Krafft[6] have reported the formation of a hydronitrate of benzene seleninic acid, $C_6H_5SeO_2H\cdot HNO_3$; Jackson[7] has reported the same phenomenon with benzyl seleninic acid, $C_6H_5CH_2SeO_2H$, and Shaw and Reid[8] with methyl seleninic acid, CH_3SeO_2H, and with ethyl seleninic acid, $C_2H_5SeO_2H$. So far as we can discover, however, there is no record of the production of hydronitrates of the selenoxides, C_6H_5SeOR. We have studied the formation of a number of these selenoxides by a variety of methods, have prepared the hydronitrates of some of them and have evolved a theory for the mechanism of the rather unusual action of the halogen acids upon them.

By the treatment of the sodium salt of selenophenol, C_6H_5SeNa, with alkyl halides, we have prepared the following seleno-ethers: (1), $C_6H_5SeCH_3$;[9] (2), $C_6H_5SeC_2H_5$; (3), $C_6H_5SeC_5H_{11}$ (*iso*); (4), $C_6H_5SeC_6H_5$.[9]

The last compound was also procured as a by-product in the preparation of selenophenol by redistillation of the high-boiling fraction. We have treated all of these substances with a number of oxidizing agents: with fuming nitric acid, with chromic acid, with potassium permanganate and with hydrogen peroxide. Hydrogen peroxide has no effect, due probably to the small solubility of the substances in water. Chromic acid in acetic acid solution produces tarry mixtures impossible to purify. Nitric acid and potassium permanganate, however, give substances that

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[4] Lecher and Simon, *Ber.*, 55, 2426 (1922).

[5] Brand and Wirsing, *Ber.*, 46, 822 (1913).

[6] Stoecker and Krafft, *Ber.*, 39, 2200 (1906).

[7] Jackson, *Ann.*, 179, 13 (1875).

[8] Shaw and Reid, THIS JOURNAL, 48, 520 (1926).

[9] Prepared by other workers.

can be separated either as the hydronitrates or as chlorine addition products. These latter are not derivatives of selenoxides.

Preparation of Materials

Preparation of Selenophenol, C_6H_5SeH.—This compound was prepared by the Grignard reaction according to the method of Taboury[10] with the following modifications. After treating phenylmagnesium bromide with selenium and decomposing the intermediate formed with cold hydrochloric acid, we separated the ether layer, extracted the solution with more ether and combined the ether extracts. These we shook up with one equivalent of sodium hydroxide, calculated on **the** basis of the total amount of selenium used, and dissolved in water to make a 25% solution. The ethereal extracts were then dried with calcium chloride, the ether was evaporated and from the residue were recovered by distillation diphenyl diselenide and considerable quantities of diphenyl monoselenide, boiling at 303°. The sodium hydroxide solution was then acidified with a slight excess of concentrated hydrochloric acid, cooled and extracted three times with ether. The residue recovered from the ether consisted of almost pure selenophenol, b. p. 182°, which was further purified by distillation.

Preparation of the Seleno-Ethers, C_6H_5SeR.—The methyl derivative, $C_6H_5SeCH_3$, was prepared by the method of Pope and Neville;'' the others by dissolving selenophenol in one equivalent of sodium hydroxide in the minimum quantity of water, adding 50 cc. of absolute alcohol and then the alkyl halide. The mixture was refluxed for fifteen minutes, diluted with four times its volume of cold water, extracted three times with ether, the ether separated, washed with water, dried over calcium chloride and distilled off. The remaining oils were rectified. Methyl iodide was used for the methyl derivative and the bromides of the other alkyls. The experiments are summarized in Table I.

TABLE I

PREPARATION OF THE SELENO-ETHERS

C_6H_5SeR, R	Seleno-phenol, g.	Halide, g.	Yield, g.	%	B. p., °C.	Analysis for Se, Calcd.	Found
C_2H_5	10	20	8.5	72	214–216	42.44	42.35
C_5H_{11}, *iso*	18	20	22.5	86.5	105°(3 mm.)	34.84	34.24
C_6H_5[a]	10	10	3.5	24	303°	...	...

[a] Butyl alcohol was used as a solvent with the phenyl derivative.

Diphenyl Selenium Oxide, $(C_6H_5)_2SeO$.—This substance was used in checking, by analogy, the constitution of our products. We prepared it from diphenyl selenium dichloride, $(C_6H_5)_2SeCl_2$, and sodium hydroxide by Krafft and Vorster's method[12] and also from diphenyl selenoxide hydronitrate. 1.75 g. of $(C_6H_5)_2SeO:HNO_3$ was treated with sodium carbonate and extracted with alcohol according to the procedure outlined on p. 1185 and summarized in Table III. A white, granular solid was obtained which was recrystallized from dry benzene; yield of crude product, theoretical; m. p. 106–108°.

Anal. Calcd. for $C_{12}H_{10}SeO$: Se, 31.73. Found: Se, 31.86.

Analyses for chlorine were accomplished by dissolving weighed samples in water and precipitating silver chloride from the slightly acidified solution with 0.1 N silver nitrate solution. Selenium analyses were made by

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[10] Taboury, *Ann. chim. phys.*, **15**, 5 (1908).

[11] Pope and Neville, *J. Chem. Soc.*, 81, 1553 (1902).

[12] Krafft and Vorster, *Ber.*, 26, 2818 (1893).

Shaw and Reid's method,[13] the improved directions for which have been published since the completion of our work.[14]

The Action of Nitric Acid on the Seleno-Ethers.—Methylphenyl, ethylphenyl and *iso*-amylphenyl selenides react with fuming nitric acid violently in the cold, with evolution of much heat and oxides of nitrogen. The reaction mixtures were heated on the steam-bath until no more NO_2 was evolved. The methyl derivative only, however, gives a crystalline solid, which comes out of the reaction mixture in white plates or needles, on evaporation and cooling, consists of the hydronitrate of methylphenyl selenium oxide, $C_6H_5SeOCH_3 \cdot HNO_3$ and melts at 97°. The other two compounds gave water soluble oils which are insoluble in organic solvents and decompose too easily to be purified by distillation (ethylphenyl selenoxide hydronitrate decomposes at 110" under 3 mm. pressure). Consequently their constitution can only be assumed by analogy to the methyl and phenyl derivatives. If heated much above 100°, all three compounds decompose, with evolution of NO_2, leaving behind diphenyl diselenide. melting at 63°, which we identified by a mixed melting point with a sample of diphenyl diselenide obtained as a by-product in the preparation of selenophenol. An attempt to identify the other products of the decomposition, made with the methyl derivative, was unsuccessful, so that we cannot at present write an equation for this reaction. The details of these processes will be found in Table II.

TABLE II

PREPARATION OF THE SELENOXIDE HYDRONITRATES

$C_6H_5SeOR \cdot HNO_3$

R	Seleno-ether, g.	HNO_3, cc.	Yield, g.	Yield, %	M. p., °C.	Analysis for Se Calcd.	Analysis for Se Found	Physical form and color
CH_3	15	16	21	64	97	31.38	31.24–31.21	White needles or plates
C_2H_5	15	20	..	..	..	...	...	Colorless oil
C_5H_{11}	30	40	..	..	..	...	...	Colorless oil
C_6H_5	15	20	15.5	77	97	25.16	25.47–25.47	White needles

The oils obtained were treated directly by the process of Table III.

When these hvdronitrates are treated in water solution with sodium carbonate one mole of the carbonate is taken up, carbon dioxide is evolved and evaporation to dryness and extraction with alcohol or benzene yields oils which are undoubtedly the selenoxides, C_6H_5SeOR, but which again are too little soluble and decompose too easily to be purified, When these oils are treated with concentrated hydrochloric acid (the

TABLE III

PREPARATION OF THE DICHLORIDES, $C_6H_5SeCl_2R$, BY THE ACTION OF Na_2CO_3 AND HCl ON THE HYDRONITRATES OR OXIDES

R	Starting compound, g.	Yield g.	%	Mixed m. p.. °C.
CH_3	$C_6H_5SeOR:HNO_3$ 20	10	97	122 (dec.)
C_2H_5	(Unpurified oil from Table II)			6445
C_5H_{11}	(Unpurified oil from Table II)			(Gave benzene seleninic acid, $C_6H_5SeO_2H$, mixed m. p., 121–122°)
C_6H_5	$C_6H_5SeOR:HNO_3$ 2	1	77	142 (dec.)"
C_6H_5	$(C_6H_5)_2SeO$ 2	1.4	57	142 (dec.)[a]

[a] Krafft and Vorster report a melting point of 178° (dec.) for this substance.

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[13] Private communication of Edwin H. Shaw.

[14] Shaw and Reid, THIS JOURNAL, 49,2330 (1927).

iso-amyl derivative could be dissolved in benzene and saturated with hydrogen chloride gas) they are converted to white solids, crystallizable from benzene, xylene, alcohol or dry ether, which, except the iso-amyl derivative, analyze for the dichlorides, $C_6H_5SeCl_2R$. The methyl derivative was readily reconverted to the hydronitrate by dissolving it in concentrated nitric acid, a reaction which is typical of the selenoxides.[12] Impure ethylphenyl selenium dichloride decomposed rapidly on standing in a desiccator and this method of preparing it was consequently abandoned in favor of the better one described below. All of these procedures are summarized in Table **III,** which includes for convenience the phenyl derivative described below.

The compounds were identified by taking mixed melting points with samples prepared by the method outlined in Table IV.

Because of our inability to obtain isolable intermediates, the reactions described above were not entirely satisfactory. In order to check them we decided to carry them out upon the phenyl analog of the compounds we had used, namely, diphenyl diselenide, $(C_6H_5)_2Se$, which gave promise of better results. In fact, diphenyl selenium oxide had already been described by Krafft and Vorster,[12] but it had never been prepared by oxidation with nitric acid and its hydronitrate was unknown. In our first attempt we oxidized the high-boiling fraction (295–305') of the by-products obtained in making selenophenol by the Grignard reaction, which should have consisted chiefly of diphenyl selenide.[10] It gave, however, a mixture of three solids, melting at 95–98°, 130–135°, and 226–228°, respectively, which we did not attempt to identify. We then prepared pure diphenyl selenide from sodium selenophenolate and bromobenzene (see Table I) and from this were able to procure a hydronitrate, $(C_6H_5)_2SeO{\cdot}HNO_3$, which melted at 97° (see Table II). Sodium carbonate treatment gave from this Krafft and Vorster's diphenyl selenium oxide, melting at 106–log°, and solution of the latter in dry benzene and saturation with hydrochloric acid, or simply treatment with concentrated hydrochloric acid, gave the dichloride, $(C_6H_5)_2SeCl_2$ (Table III). The last substance was unstable, beginning to decompose at 137° and melting at 142°. We have, therefore, an analogy for the reactions described in the foregoing paragraphs, equations for which may be written as follows.

$$C_6H_5SeR + 3HNO_3 = C_6H_5SeOR{\cdot}HNO_3 + 2NO_2 + H_2O \qquad (I)$$

$$2C_6H_5SeOR{\cdot}HNO_3 + Na_2CO_3 = 2C_6H_5SeOR + 2NaNO_3 + CO_2 + H_2O \qquad (II)$$

$$C_6H_5SeOR + 2HCl = C_6H_5SeCl_2R + H_2O \qquad (III)$$

The suggested mechanism for this last reaction is given under another heading.

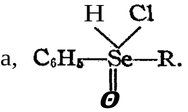
The Action of Potassium **Permanganate** on the **Seleno-Ethers.**—Methylphenyl, ethylphenyl, *iso*-amylphenyl and diphenyl selenides were dissolved in glacial acetic acid and oxidized at room temperature with a saturated aqueous solution containing one equivalent of potassium permanganate. No selenoxide except the diphenyl could be isolated by this process but by filtering, cooling the reaction mixture in ice and saturat-

TABLE IV

PREPARATION OF THE DICHLORIDES, $C_6H_5SeCl_2R$, BY THE ACTION OF $KMnO_4$ AND HCl ON THE SELENO-ETHERS

R	Seleno-ether, g.	HAc, cc.	$KMnO_4$, g.	Yield, g.	%	Crystallizing solvent	M. p., °C.	Analysis for Cl Calcd.	Found
CH_3	20	100	12.2	18.6	68.5	Xylene	122	29.3	29.1
							(dec.)		29.6
C_2H_5	10	50	3.7	2	13	Ether	64–65	27.7	27.8
C_5H_{11}	6.3	33	2.3	6.3	76	EtOH	80	23.8	24.0
C_6H_5	13.8	50	3.8	7.1	25	Xylene	142	23.6	23.7
							(dec.)		23.8

ing with hydrogen chloride there was precipitated in every case a white solid that could be filtered off and recrystallized. These white solids turned out to be the dichlorides described above. For the details of these procedures see Table IV.

The formation of such compounds is rather unexpected. They could not be formed by the direct action of chlorine produced from the oxidation of hydrochloric acid by the permanganate, because a spot test on filter paper was made in each case and the absence of free permanganate established before the hydrochloric acid was added. They must, therefore, have been formed by the action of the acid upon an intermediate oxidation product, in all probability the selenoride. One would anticipate, from the behavior of nitric acid, the formation of hydrochlorides of the general formula,  $C_6H_5\text{—}\overset{H\quad Cl}{\underset{\overset{\|}{O}}{Se}}\text{—}R$. In order to prove their constitution we treated the methyl and phenyl seleno-ethers with dry chlorine, using dry ether as a solvent, and in each case obtained the same type of dichloride, $C_6H_5SeCl_2R$, that we had by the other methods.

$$C_6H_5SeR + Cl_2 = C_6H_5SeCl_2R \qquad \text{(IV)}$$

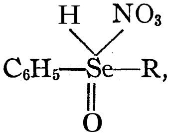
The ethyl and *iso*-amyl derivatives decomposed under the action of chlorine, evolving hydrochloric acid, so that their constitution could not be checked in the same way.

TABLE V

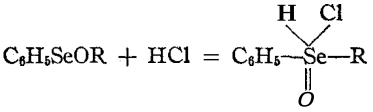
PREPARATION OF THE DICHLORIDES BY THE DIRECT ACTION OF CHLORINE ON THE SELENO-ETHERS

R	Seleno-ether, g.	Yield, g.	Yield, %	Mixed m. p., °C.
CH_3	9	7	56.5	122 (dec.)
C_6H_5	15	16.5	84	142 (dec.)

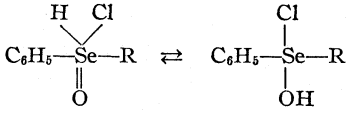
Discussion of Results

Aromatic seleno-ethers differ from the corresponding sulfur compounds in that they do not oxidize readily to the hexavalent condition but, under similar conditions, produce compounds corresponding to the sulfoxides rather than to the sulfones. This is probably due to the fact that oxidized selenium in these compounds has certain basic characteristics, adding nitric acid readily to produce loose molecular compounds of the type,  $C_6H_5\text{—}\overset{H\quad NO_3}{\underset{\overset{\|}{O}}{Se}}\text{—}R$, in which the selenium is hexavalent and further oxidation is impossible. By neutralizing the acid with a base, oxidation to the hexavalent state can then be carried to completion and selenones, $C_6H_5SeO_2R$, are obtained.[12] The acid addition products are evidently of the nature of salts, for they ionize readily in water solution to give the nitrate ion and presumably a positive ion, $(C_6H_5SeHOR)^+$.

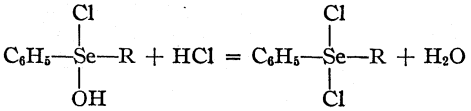
Hydrochloric acid does not form addition products but converts the selenoxides to dichlorides. In order to correlate this behavior with the addition of nitric acid to the oxides, we assume that an addition product with the hydrochloric acid first forms, but immediately rearranges to a tetravalent hydroxyl derivative, the hydroxyl group of which is then capable of reacting with another molecule of hydrochloric acid to form the dichloride.



$$C_6H_5SeOR + HCl = C_6H_5-\overset{H\quad Cl}{\underset{\underset{O}{\|}}{Se}}-R \qquad (V)$$



$$C_6H_5-\overset{H\quad Cl}{\underset{\underset{O}{\|}}{Se}}-R \rightleftarrows C_6H_5-\overset{Cl}{\underset{OH}{Se}}-R \qquad (VI)$$



$$C_6H_5-\overset{Cl}{\underset{OH}{Se}}-R + HCl = C_6H_5-\overset{Cl}{\underset{Cl}{Se}}-R + H_2O \qquad (VII)$$

The hydrochloric acid in the last reaction may even be obtained at the expense of a molecule of the original addition product, for diphenyl selenoxide, when recrystallized from concentrated hydrochloric acid, gave a product with no sharp melting point; this may well have been a mixture of the selenoxide and the dichloride, for it was readily converted completely to the dichloride by further treatment with concentrated hydrochloric acid.

The dichlorides also appear to be salts, ionizing readily in water solution.

Summary

By the action of alkyl halides on sodium selenophenolate the authors have prepared two new and two known alkyl or aryl phenyl seleno-ethers. They have studied the action of several oxidizing agents upon these compounds and have prepared some nitric acid addition products of the oxides formed. The action of hydrochloric acid on the oxides has also been investigated, the constitution of the products proved and a mechanism for the reaction proposed.

ANNANDALE-ON-HUDSON, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

FRIEDEL AND CRAFTS' REACTION IN THE PYRIDINE SERIES

BY C. M. JEPHCOTT

RECEIVED DECEMBER 14, 1927 PUBLISHED APRIL 5, 1928

Engler[1] and Wolffenstein and Hartwich[2] made unsuccessful attempts to condense acid chlorides with pyridine in the presence of aluminum chloride. When phthalic anhydride is used with pyridine in benzene solution and aluminum chloride, only phthalic acid is obtained because an addition compound of phthalic anhydride and pyridine is formed which prevents the reaction and even prevents the formation of o-benzoylbenzoic acid. It was thought that if the hydrochloric acid salt of pyridine or the alkyl halide or acyl halide addition compound were used, there would be no addition compound with the acid anhydride. These compounds, however, were found to be very slightly soluble in benzene or carbon disulfide and after the Friedel and Crafts' reaction only o-benzoylbenzoic acid was obtained from the benzene solution and phthalic acid from the carbon disulfide solution. When these addition compounds of quinoline were used the results were also unsatisfactory.

Bernthsen and Mettegang,[3] Jeiteles,[4] and Kirpal[5] have studied the reaction of quinolinic anhydride with benzene and aluminum chloride. Just,[6] Fulda[7] and Halla[8] used toluene instead of benzene and Halla also used xylene. In each case only derivatives of picolinic acid were obtained and no derivatives of nicotinic acid. Derivatives of picolinic acid are easily distinguished from derivatives of nicotinic acid by the red color given when they are dissolved in aqueous or alcoholic solution of ferrous sulfate.

In the present research, the work of Just, Fulda and Halla has been extended using naphthalene, acenaphthene and diphenyl, respectively. In each case only derivatives of picolinic acid were obtained and in the case of naphthalene both the a-naphthoyl and β-naphthoyl derivatives were formed. The yield never exceeded 22%. Phenylpyridophthalide has also been used in the Friedel and Crafts' reaction and in each case the product was a derivative of picolinic acid and there was no evidence of the formation of a ketone. This corresponds with the results of King[9] who used phthalides. The yields were about 25–30%.

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[1] Engler, *Ber.*, **24, 2525 (1891).**

[2] Wolffenstein and Hartwich, *Ber.*, **48,2043 (1915).**

[3] Bernthsen and Mettegang, *Ber.*, **20,1208 (1887).**

[4] Jeiteles, Monatsh., **17, 515 (1896).**

[5] Kirpal, *ibid.*, **27, 371 (1906); 31, 295 (1910).**

[6] Just, *ibid.*, **18, 452 (1897).**

[7] Fulda, *ibid.*, **21, 981 (1900).**

[8] Halla, *ibid.*, **32, 747 (1911).**

[9] King, THIS JOURNAL, **49, 562 (1927).**

In studying the Friedel and Crafts' reaction using the acid chlorides of the monomethyl esters of quinolinic acid, it has been shown that the ester of m. p. 108° gave two products and is, therefore, a mixture.

Quinolinic Anhydride with Aluminum Chloride and Naphthalene in Benzene Solution.—Thirty g. of anhydride and 30 g. of naphthalene were partially dissolved in 200 cc. of benzene and 75 g. of aluminum chloride were added. After heating for twenty-four hours on the water-bath, dilute hydrochloric acid was added and the benzene and excess naphthalene were removed by distillation with steam. The remaining tar was boiled several times with hydrochloric acid and the acid solutions were combined. Addition of cupric chloride solution to the combined acid solutions gave a grayish-blue precipitate which was filtered off and the filtrate on standing gave a bright blue precipitate. These precipitates were suspended separately in hot water, decomposed by hydrogen sulfide and filtered. The filtrates were evaporated to dryness and the filtrate from the bright blue precipitate gave only quinolinic acid. The filtrate from the first precipitate gave a residue part of which was soluble in dilute acetic acid, m. p. 145°, and the insoluble part melted at 155°. The total yield was 22% but much the larger part melted at 145° and qualitative tests showed both to be derivatives of picolinic acid. The silver salt of the product melting at 155° was analyzed.

Anal. Calcd. for $C_{17}H_{10}O_3NAg$: Ag. 28.1. Found: 28.1.

The product melting at 145° was fused with sodium hydroxide and gave β-naphthoic acid. The latter is, therefore, β-naphthoylpicolinic acid (1,2) and the former α-naphthoylpicolinic acid (1,2).

Quinoline Anhydride with Aluminum Chloride and Acenaphthene in Benzene Solution.—Ten g. of quinolinic anhydride, 11 g. of acenaphthene, 23 g. of aluminum chloride, and 100 cc. of benzene were used. The product obtained from the decomposition of the cupric chloride precipitate was recrystallized from dilute acetic acid; m. p. 168–169°; yield, 10%. This product was shown to be a derivative of picolinic acid and is believed to be 4-acenaphthoylpicolinic acid, as Lorriman[10] has shown that phthalic anhydride reacts with acenaphthene to give the 4-acenaphthoyl derivative.

Quinolinic Anhydride with Aluminum Chloride and Diphenyl in Benzene Solution.—Three g. of quinolinic anhydride, 5 g. of diphenyl, 10 g. of aluminum chloride and 100 cc. of benzene were used. This yielded a yellow solution and a bright yellow precipitate. The solution after treatment with cupric chloride gave 2.5 g. of benzoylpicolinic acid. The yellow precipitate after solution in sodium hydroxide and acidification was a white, flaky precipitate; m. p. 170–171°; yield, 1 g. On fusion with sodium hydroxide this compound gave p-phenylbenzoic acid and is, therefore, p-phenylbenzoylpicolinic acid (1,2).

Phenylpyridophthalide with Aluminum Chloride and Benzene.—Three g. of phenylpyridophthalide was partially dissolved in 100 cc. of benzene and 10 g. of aluminum chloride added. After removal of benzene the solution yielded 1.2 g. of white, needle-like crystals. On recrystallization these melted sharply at 155°. This compound is diphenylmethylpicolinic acid (1.2).

Anal. Calcd. for $C_{19}H_{14}O_2NAg$: Ag, 27.2. Found: 27.0.

The Monomethyl Esters of Quinolinic Acid.—Two monomethyl esters of quinolinic acid have been described, m. p. 123° and m. p. 108°, but there has been some confusion about their identification.

These esters were prepared from quinolinic anhydride and after separation of the ester of m. p. 123° a much smaller amount of the ester of m. p. 108° was obtained.

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[10] Lorriman, THIS JOURNAL, 47, 211 (1925).

The first ester was dissolved in thionyl chloride, the solution evaporated to dryness and toluene and aluminum chloride added. The product from this Friedel and Crafts' reaction was *p*-tolylpicolinic acid (1,2), confirming the view that this ester of m. p. 123° was α-monomethyl quinolinate.

When the second ester was dissolved in thionyl chloride and the resulting acid chloride treated with benzene and aluminum chloride, the product melted at 170°. Kirpal in the same experiment had obtained a product with m. p. 176° which he called α-benzoylnicotinic acid. On treating the product of m. p. 170' with hot water two fractions were obtained. The soluble part was benzoylnicotinic acid (1,2) and the insoluble part melted at about 285°, and as the latter was not a derivative of picolinic acid it was assumed to be benzoylnicotinic acid (1,2). This experiment showed that the substance melting at 108° was a mixture of the two monomethyl quinolinates and that the substance melting at 176° contained considerable amounts of benzoylpicolinic acid (1,2). It also showed that benzoylnicotinicacid melted about 100° higher than had previously been reported by Kirpal.

Various methods were used in an attempt to prepare diphenylpyridophthalide. Quinolinic anhydride, benzene, aluminum chloride and acetic anhydride gave only benzoylpicolinic acid (1.2). The acetyl derivative of benzoylpicolinicacid with benzene and aluminum chloride gave equally unsatisfactory results. Oxidation of diphenylmethylpicolinic acid (1,2) gave a small quantity of a material which may have been the desired substance but there was too little of it for identification.

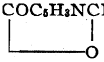
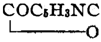
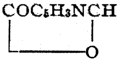
The following table indicates the preparation of the substances obtained in the above experiments and some of their derivatives as well as the preparation of some other pyridine derivatives.

TABLE I

PREPARATION AND PROPERTIES OF COMPOUNDS

Name	Formula	Preparation	Remarks
β-Naphthoylpicolinic acid (1,2)	$C_{10}H_7COC_5H_3NCO_2H$	Quinolinic anhydride, $AlCl_3$ and naphthalene in benzene soln.	M. p. 145°. Chlorohydrate, m. p. 172–173°. Methyl ester, m. p. 80–82°. Hydrate from hot water, m. p. 109°
a-Naphthoylpicolinic acid (1,2)	$C_{10}H_7COC_5H_3NCO_2H$	Quinolinic anhydride, $AlCl_3$ and naphthalene in benzene soln.	M. p. 155°. Chlorohydrate, m. p. 179–180°. Methyl ester, m. p. 100–101°
4-Acenaphthoylpicolinic acid (1,2)	$C_{12}H_9COC_5H_3NCO_2H$	Quinolinic anhydride, $AlCl_3$ and acenaphthene in benzene soln.	M. p. 168–169°. Chlorohydrate, m. p. 175°. Methyl ester, m. p. 113–114°. Hydrate from hot water m. p. 121°
p-Phenylbenzoylpicolinic acid (1,2)	$C_6H_5C_6H_4COC_5H_3NCO_2H$	Quinolinic anhydride, $AlCl_3$ and diphenyl in benzene soln.	M. p. 170–171°
Benzoylnicotinic acid (1,2)	$C_6H_5COC_5H_3NCO_2H$	Monomethyl quinolinate, m. p. 108°, with thionyl chloride and then benzene and $AlCl_3$	M. p. 285°. Methyl ester, m. p. 87°
Dibenzoylpyridine (1,2)	$(C_6H_5CO)_2C_5H_3N$	Benzoylpicolinyl chloride with benzene and $AlCl_3$	M. p. 186–187°
Tolylbenzoylpyridine (1,2)	$C_7H_7COC_5H_3NCOC_6H_5$	Benzoylpicolinyl chloride with toluene and $AlCl_3$	M. p. 190–193°

TABLE I *(Concluded)*

Name	Formula	Preparation	Remarks
p-Tolylpyridophthalide	 $COC_5H_3NCH—C_7H_7$	Reduction of **p-tolyl**picolinic acid (1,2) by zinc in ammoniacal soln.	M. p. 144°
β-Naphthoylpyridophthalide	 $COC_5H_3NCHC_{10}H_7$	Reduction of **β-naph**thoylpicolinic acid (1,2)	M. p. 127°
Lactone of **β-carbo**hydroxy-a-pyridyl-**phenyl carbinol**	 $COC_5H_3NCHC_6H_5$	Reduction of **benzoyl**nicotinic acid (1,2)	M. p. 128°
Diphenylmethyl-**picolinic** acid (1,2)	$(C_6H_5)_2CHC_5H_3NCO_2H$	Phenylpyridophthalide with benzene and $AlCl_3$	M. p. 153°. Methyl ester, m. p. 109°
Phenyltolylmethyl-picolinic acid (1,2)	$C_6H_5C_7H_7CHC_5H_3NCO_2H$	Phenylpyridophthalide with toluene and $AlCl_3$	M. p. 161°
β-Pyridyldiphenylmethane	$C_5H_4NCH(C_6H_5)_2$	Heating diphenylmethyl-**picolinic** acid (1,2) to 170°	M. p. 78–79'

This research was carried out under the direction of Professor F. B. Allan. The author held a Studentship from the Research Council of Canada.

Summary

1. Phthalic anhydride with aluminum chloride and various addition compounds of pyridine and of quinoline showed no reaction between the phthalic anhydride and the addition compounds.

2. Quinolinic anhydride with aluminum chloride and naphthalene, acenaphthene and diphenyl, respectively, gave only the corresponding picolinic acid derivatives and no benzoylpicolinic acid except in the case of diphenyl.

3. Various derivatives of picolinic and nicotinic acids have been prepared from the monomethyl quinolinates and it has been shown that the β-monomethyl quinolinate and a-benzoylnicotinic acid, previously described, were mixtures.

4. Phenylpyridophthalide with aluminum chloride and benzene or toluene gave only derivatives of picolinic acid.

TORONTO, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

THE FORMATION OF PRIMARY AMINES FROM GRIGNARD REAGENTS AND MONOCHLORO-AMINE

BY GEORGE H. COLEMAN AND C. R. HAUSER[1]

RECEIVED DECEMBER 19, 1927 PUBLISHED APRIL 5, 1928

Comparatively few reactions of Grignard reagents with halogen compounds in which the halogen atom is attached to nitrogen have been studied. Oddo[2] prepared nitrosobenzene from nitrosyl chloride (NOCl) and phenylmagnesium bromide. Zuskine[3] has reported, however, that nitroxyl chloride (NO_2Cl) does not form nitro compounds with either phenylmagnesium bromide or ethylmagnesium bromide. Strecker[4] isolated only ammonium salts from the reaction mixtures of nitrogen trichloride with phenylmagnesium bromide and ethylmagnesium bromide. Buylla[5] failed in an attempt to prepare triethylamine by the action of iododiethylamine on ethylmagnesium bromide, the iododiethylamine being recovered almost quantitatively. Grignard[6] and his co-workers have studied the reactions of cyanogen chloride, bromide and iodide with a variety of organomagnesium halides. With cyanogen chloride the principal product is in many cases the nitrile. In such reactions the authors regard the cyanogen chloride as reacting in that form in which the chlorine is attached to carbon ($Cl—C\equiv N$). With cyanogen bromide and iodide the principal product is the corresponding halogen derivative instead of the nitrile. The halogen atoms are here regarded as being attached to nitrogen ($I—N\equiv C$ or $I—N=C<$).

The present investigation was carried out to determine the possibility of preparing primary amines directly from Grignard reagents and monochloro-amine. The results thus far obtained show that primary amines and ammonia are formed. In this reaction a variation in the yields of the products obtained with chlorides, bromides and iodides has also been observed. If the Grignard reagent be represented by RMgX, then for the same radical R, the yield of amine is greatest when X is chlorine and least when X is iodine. When X is bromine the yield of amine lies between the other two. The results with twenty-three Grignard reagents thus far used are given in Table I. It is apparent that the yield of ammonia increases as the yield of amine decreases.

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[1] This communication is an abstract of the thesis submitted by C. R. Hauser in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

[2] Oddo, *Gazz. chim. ital.*, *39*, *I*, 659 (1909).

[3] Zuskine, *Bull. soc. chim.*, *37*, 187 (1925).

[4] Strecker, *Ber.*, 43, 1131 (1910).

[5] Buylla, *Rev. real. acad. cien.* (*Madrid*), *9*, 635–653, 718–734 (1910).

[6] (a) Grignard, Bellet and Courtot, *Ann. chim.*, [9] *12*, 364 (1919); (b) Grignard and Perrichon, *ibid.*, [10] 5, 5 (1926).

TABLE I

PERCENTAGE YIELDS OF AMINES AND AMMONIA FROM MONOCHLORO-AMINE AND GRIGNARD REAGENTS

	X = Cl % yields		X = Br % yields		X = I % yields	
Reagent	RNH_2	NH_3	RNH_2	NH_3	RNH_2	NH_3
CH_3MgX	..	..	26.3	68.4	7.6	87.5
C_2H_5MgX	57.2	39.6	27.7	65.7	16.2	81.4
n-C_3H_7MgX	58.2	36.9	27.0	63.8	13.9	69.8
n-C_4H_9MgX	58.9	38.5	27.2	65.2	15.3	84.7
Iso-$C_5H_{11}MgX$	55.2	41.2	26.8	71.7	10.9	83.9
C_6H_5MgX	26.7	68.0	14.5	83.9	0.8	95.6
$C_6H_5CH_2MgX$	85.0	3.7	54.7	38.7	49.4	45.8
$C_6H_5C_2H_4MgX$	74.0	18.4	42.3	52.6	15.0	73.7

The Grignard reagents were prepared in the usual manner in ether solution and, since in each reaction with monochloro-amine an excess of the Grignard reagent was used, the variation in the yields with chlorides, bromides and iodides must have been caused by the different halogens present in the reagent.

The monochloro-amine was prepared in ether solution by a modification of the method described by Marckwald and Wille.[7] These authors found that monochloro-amine distributes itself between water and ether in the ratio of approximately one to one. The solubility of monochloro-amine in other common organic solvents is less than this.

The reaction of monochloro-amine with the Grignard reagent is rapid even at 0°, and the penetrating odor of monochloro-amine quickly disappears. The following reactions are suggested for the formation of the amines and ammonia.

$$RMgX + NH_2Cl = RNH_2 + MgXCl \qquad (1)$$
$$RMgX + NH_2Cl = RCl + MgXNH_2 \qquad (2)$$

With the Grignard reagents of the lower alkyl halides the corresponding hydrocarbon gas was evolved, as would be expected due to the secondary reaction of the excess Grignard reagent with the products.

Since, as indicated in Table I, nearly all of the monochloro-amine is accounted for in the formation of ammonia and the amine, the above reactions are the principal ones occurring. With benzylmagnesium chloride the largest yield of amine was obtained, and with phenylmagnesium iodide the lowest yield of amine with the production of the largest yield of ammonia. If the formation of ammonia is due to reaction (2), then we should expect the formation of the corresponding chloride. Thus, with phenylmagnesium iodide, in which, as mentioned, the yield of ammonia was greatest, an equivalent amount of chlorobenzene was to be expected. In this reaction chlorobenzene was isolated from the reaction products.

No indication of the presence of secondary or tertiary amines was found.

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[7] Marckwald and Wille, *Ber.*, 56, 1319 (1923).

The products obtained as the hydrochlorides were analyzed and derivatives prepared.

This work is being continued with other chloro-amines.

Experimental

Preparation of Monochloro-amine.—A solution of 200 cc. of sodium hypochlorite, made from 2 *N* sodium hydroxide and the calculated amount of chlorine (the solution remained alkaline after the addition of the chlorine), was mixed with 200 cc. of *N* ammonium hydroxide containing pieces of ice. The monochloro-amine was either extracted with ether directly or, when a more concentrated solution was desired, the mixture was distilled at 30–40° under a pressure of 15–25 mm. until about 100 cc. of distillate had collected in the receiver. A spiral condenser surrounded by ice water was used and the receiver was immersed in a freezing mixture of either ice and salt, or carbon dioxide snow and alcohol. When the latter freezing mixture was used, about 80 cc. of ether placed in the receiver retained much of the monochloro-amine which would otherwise have been lost. The ether solution was poured off, the ice melted and the solution extracted three times with ether. About 80 cc. was used for each extraction. The ether extracts were poured together and dried with calcium chloride for a few minutes, keeping the container immersed in a freezing mixture. The dry ether solutions prepared by this method contained over 100 mg. moles of monochloro-amine. Other drying agents were used but calcium chloride seemed to be very satisfactory if the drying was carried out as specified above. An analysis of the solution before and after drying showed little change in the concentration of monochloro-amine.

Analysis of the Monochloro-amine Solution.—The analysis of the monochloro-amine solution for nitrogen was carried out by adding 5 cc. of the ether solution to 15 cc. of cold concentrated hydrochloric acid contained in a small flask. When the reaction was complete the ether was removed by gentle heating and the ammonia determined by the addition of excess alkali and distillation into standard acid.

The analysis for chlorine was carried out by adding 5 cc. of the solution to an excess of sodium sulfite solution. After the completion of the reaction the ether was removed by means of a separatory funnel and the excess sulfite oxidized with potassium permanganate after acidifying with nitric acid. The chlorine content was then determined by the Volhard method.

In some cases the weight of the sample was used instead of the volume. The results of a large number of determinations showed that the ratio of nitrogen to chlorine was 1:1. The ether solutions of monochloro-amine were always colorless, thus also indicating the absence of appreciable amounts of either chlorine or nitrogen trichloride.

Reaction of Monochloro-amine with the Grignard Reagents

The reactions of monochloro-amine with the Grignard reagents were carried out by adding, slowly and with shaking, the cold, dry ether solution of monochloro-amine to the Grignard reagent, which was cooled to 0° or below. As soon as the ether solution of monochloro-amine came in contact with the Grignard reagent a precipitate formed, leaving at the end a more or less gelatinous mass. In the reactions with organomagnesium iodides a brown coloration always appeared immediately upon the addition of the monochloro-amine solution. After the completion of the reaction, the flask containing the mixture was connected to a condenser with an adapter at the lower end dipping under dilute hydrochloric acid. The excess Grignard reagent was then decomposed by the addition of water through a dropping funnel, and the basic mixture either treated directly with steam, or first brought into solution with acid, and then made alkaline and steam distilled until no more basic substance passed over. The ether and aqueous layers of the distillate were shaken together and, after separating, the hydrochloric acid solution was evaporated to dryness on a water-bath. After drying thoroughly in a vacuum desiccator, the amine hydrochloride was dissolved in *n*-**butyl** alcohol and the undissolved ammonium chloride filtered off. The amine hydrochloride was obtained by evaporating the alcohol on a water-bath.

The purity of the hydrochlorides was determined by analysis and the amines were identified by preparing derivatives and taking mixed melting points with known compounds.

Phenylmagnesium Iodides with Monochloro-axnine.—A solution of **120 mg.** moles of monochloro-amine in **300** cc. of ether was added to excess of the Grignard reagent products: $C_6H_5NH_2HCl$, **0.13** g.; NH_4Cl, **6.13.** g.

The ether layer of the distillate was dried with calcium chloride and fractionated. About **4** g. of chlorobenzene, several grams of benzene, iodobenzene and a residue of diphenyl were obtained. The 4 g. of chlorobenzene is only about a thiid of that which would theoretically be present according to equation **(2)** but the pure product completely freed from the other fractions, which were much larger, does not represent all of this compound present in the reaction mixture.

Preparation of Phenylethyl **Iodide.**[9]—A solution of **200** g. of sodium iodide in **100** cc. of acetone was mixed with **137** g. of phenylethyl chloride. After boiling for four hours, about three-fourths of the acetone was distilled off and the remaining liquid poured into twice its volume of cold water. The oil was separated and washed successively with sodium bisulfite solution, water, sodium carbonate solution and again with water. It was then dried with calcium chloride and fractionated in *vacuo*. There **was** a rather large low boiling fraction. The fraction boiling at 125–128° at **18–20** mm. **was** analyzed and used in the preparation of the Grignard reagent.

Anal. **(Parr** bomb). Subs., **0.1757, 0.2927: 7.44, 12.37** cc. of **0.1010** *N* $AgNO_3$. Calcd. for C_8H_9I: I, **54.71.** Found: **54.27, 54.17.**

Phenylethyl iodide has been prepared by **Heidelberger**;[10] the boiling point, however, did not indicate a pure product.

Preparation of **Benzyl** Iodide.''—A solution of **100** g. of sodium iodide in **500** cc. of acetone was mixed with **63** g. of benzyl chloride and **refluxed** for one hour. The mixture was poured into **1500** cc. of water and the oil separated and placed in an ice-salt bath until it solidified. By recrystallizing from alcohol a yield of **38 g.** of benzyl iodide (m. p. **24°**) was obtained.

Summary

Monochloro-amine reacts with Grignard reagents to form primary amines and ammonia. The yields of amines are greatest with organomagnesium chlorides, less with bromides and least with iodides.

IOWA CITY, IOWA

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[8] Since the yield of ammonia was greatest in this reaction and chlorobenzene was isolated from the reaction products, the details are here given.

[9] Most of the reagents used are readily obtainable. The two described here are somewhat less common.

[10] Heidelberger, J. *Biol. Chem.*, **21, 466 (1915).**

[11] Kumpf, *Ann.,* 224, 126 (1884).

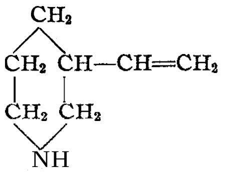
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

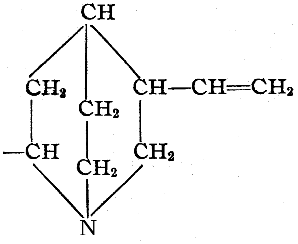
β-VINYL PIPERIDINE

BY R. MERCHANT[1] WITH C. S. MARVEL

RECEIVED DECEMBER 27, 1927 PUBLISHED APRIL 5, 1928

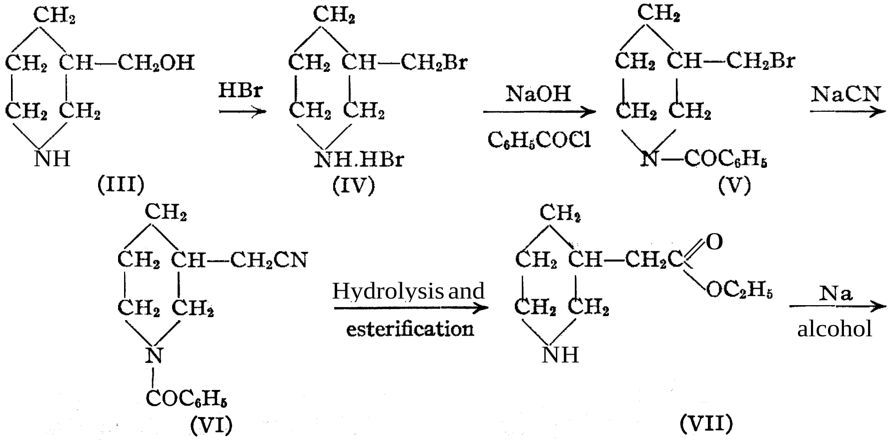
β-Vinyl piperidine (I) is of interest because of its structural relationship to the quinuclidine nucleus (II) of the natural alkaloids of the cinchonine and quinine group.


(I)


(II)

The isomeric a-vinyl derivative of piperidine has been prepared and characterized.[2] Lipp and Ladenburg[3] have had some controversy over a compound which is thought to be N-methyl-β-vinyl piperidine. However, the structure of this product has not been proved by a complete synthesis.

β-Vinyl piperidine has been synthesized from β-piperidyl carbinol (III) by the following reactions



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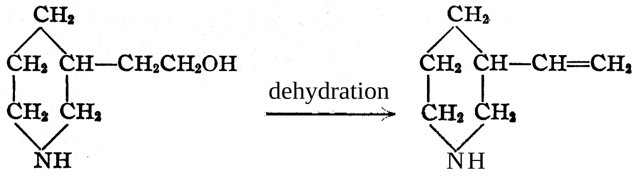
[1] This communication is an abstract of a thesis submitted by Raymond Merchant in partial fulfilment of the requirements for the degree of Doctor of Philosophy, in chemistry, at the University of Illinois.

[2] Ladenburg, *Ber.*, 22, 2587 (1889).

[3] The references to this work can be obtained from the article by Lipp and Widnmann, *Ann.*, 409, 79 (1915).



(VIII)

β-**Piperidyl** carbinol was obtained by the method of **Sandborn** and **Marvel.**[4] It was **refluxed** with constant boiling hydrobromic acid and evaporated to dryness to give a crude 8-piperidylmethyl bromide **hydrobromide** (IV), which in turn was converted to **N-benzoyl-*β*-piperidyl** methyl bromide (V). An unsuccessful attempt was made to obtain this compound by preparing N-benzoyl-8-piperidyl carbinol and then reacting with phosphorus tribromide. The bromide would not crystallize and could not be distilled without decomposition. The crude product was used in the preparation of N-benzoyl-8-piperidyl acetonitrile (VI). This compound was also very difficult to obtain pure. It was hydrolyzed by boiling hydrochloric acid and the crude amino acid was esterified with ethyl alcohol. The **ethyl-*β*-piperidyl** acetate (VII) thus obtained was isolated in a very pure condition. The reduction of the ester to **2-*β*-piperidylethanol-1** (VIII) was accomplished with **sodium** and alcohol.

The dehydration of the primary alcohol was brought about by heating a toluene solution of the amino alcohol with phosphorus **pentoxide.**[5] The same procedure was used to convert 8-piperidyl carbinol to ***β*-methylene** piperidine. Only small amounts of these two unsaturated **amines** were obtained and they could not be purified as carefully as is desirable before the physical properties were determined. However, they were characterized beyond doubt by converting them into solid salts which could be crystallized and thus purified.

Experimental **Part**

Derivatives of ***β*-Piperidyl Carbinol.**—***β*-Piperidyl** carbinol was dissolved in dilute hydrochloric acid and this solution was treated with a slight excess of platinum chloride. The solution was evaporated until **crystals** appeared and then allowed to stand until crystallization was complete. The crystals were filtered and dried overnight in a desiccator over phosphorus pentoxide; m. p. **174° (uncorr.), decomp.**

Anal. Subs., **0.1129;** Pt, **0.0338.** Calcd. for $(C_6H_{13}ON)_2H_2PtCl_6.H_2O$: Pt, **29.96.** Found: **Pt, 29.9.**

The molecule of water of hydration is lost when the salt stands over phosphorus pentoxide for about two weeks.

Anal. Subs., **0.1496, 0.0985;** Pt, **0,0453, 0.0300.** Calcd. for $(C_6H_{13}ON)_2H_2PtCl_6$: Pt, **30.49.** Found: Pt, **30.28, 30.46.**

The **chloro-aurate** of ***β*-piperidyl** carbinol was obtained by mixing a solution of the

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[4] **Sandborn** with Marvel, THIS JOURNAL, **50, 565 (1928).**

[5] Compare **Löffler and Remmler,** *Ber.*, **43, 2053 (1910).**

hydrochloride with a 10% solution of gold chloride, evaporating until crystals appeared and then cooling in an ice-bath. The crystals were separated by filtration and recrystallized from 70% alcohol. The product melted at 153–154° with the evolution of gas.

Anal. Subs., 0.1816; Au, 0.0791. Calcd. for $(C_6H_{13}ON)HAuCl_4$: Au, 43.3. Found: Au, 43.5.

N-Benzoyl-β-piperidyl Carbinol.—To a solution of 9 g. of β-piperidyl carbinol in 100 cc. of water was added, simultaneously during a period of one hour, a solution of 6 g. of potassium hydroxide in 50 cc. of water and 11 g. of benzoyl chloride. Vigorous stirring was maintained during the addition and continued until the odor of benzoyl chloride disappeared. The product was then extracted with benzene and distilled. The product boiled at 213° under 5 mm. On redistillation under very high vacuum (0.01–0.02 mm.) two fractions were obtained. The first fraction (2.7 g.) boiled below 153°; $n_D^{25} = 1.5690$. On standing it solidified. The second fraction (6 g.) boiled at 153–160"; $n_D^{25} = 1.5692$. It did not solidify.

The solid compound was recrystallized from an acetone-ether mixture and obtained as a white crystalline product, m. p. 80–81°.

Anal. Subs., 0.1978; CO_2, 0.5178; H_2O, 0.1398. Calcd. for $C_{12}H_{17}NO_2$: C, 71.19; H, 7.83. Found: C, 71.38; H, 7.90.

N-Benzoyl-β-piperidyl Acetonitrile.—Twenty g. of β-piperidyl carbinol was refluxed with 160 g. of 48% hydrobromic acid for about four hours. The solution was evaporated to dryness under reduced pressure, the residue was taken up in another 160g. portion of 48% hydrobromic acid and the solution was refluxed for four hours. The mixture was again evaporated to dryness and the residue was boiled with ethyl acetate and filtered.

The crude solid, which consisted mainly of 8-piperidyl-methyl bromide hydrobromide was suspended in 100 cc. of ether and decomposed with a solution of 10 g. of potassium hydroxide in 50 cc. of water. The temperature was held at 0–10° by means of an ice-salt bath. The ether solution of the amine was then treated with 30 g. of benzoyl chloride dissolved in 100 cc. of dry ether and the mixture was stirred and treated with 25 g. of finely powdered potassium hydroxide to remove the hydrogen chloride formed by the reaction.

The ether suspension was treated with ice water to dissolve the excess alkali and salts, the ether layer separated and the aqueous layer extracted once with about 100 cc. of chloroform. The ether and chloroform solutions were mixed and evaporated until the solvents were removed. The residual material was treated with a solution of 6 g. of sodium cyanide in 40 cc. of alcohol and 12 cc. of water and the mixture was refluxed for about 48 hours. The solution was evaporated to dryness and the product extracted from the salt by means of 60 cc. of ethyl acetate. The solvent was evaporated and the residue distilled. The yield of product, b. p. 165–175° (at about 0.1 mm.), was 13–15 g. (33–38% of the theoretical amount). There was 3 g. of lower-boiling material and 4 g. of higher-boiling material which also was mainly the desired product.

The N-benzoyl-8-piperidyl acetonitrile thus obtained is not entirely free from the amide, as is shown by the low values for carbon in the analysis and by the differences between the calculated and observed M_D values.

Anal. (Total carbon.) Subs., 0.4050, 0.3945; CO_2, 648, 627 cc. (T, 28°; P, 739 mm.). Calcd. for $C_{14}H_{16}N_2O$: C, 73.7. Found: C, 72.7, 72.2. The physical constants on a sample of this purity were: $d_4^{20} = 1.1056$; $n_D^{20} = 1.5602$; M_D, calcd., 64.64; found, 66.69.

Ethyl β-Piperidyl Acetate.—Twenty g. of crude N-benzoyl-β-piperidyl acetonitrile was boiled under reflux with 100 cc. of concd. hydrochloric acid for about six hours.

The mixture was cooled and the benzoic acid was removed by extraction with ether. The solution was then evaporated under reduced pressure until all of the water was removed.

The viscous residue was treated with 100 cc. of a 2% solution of dry hydrogen chloride in absolute alcohol and refluxed for about eighteen hours. The solution was evaporated to dryness under reduced pressure. The ester hydrochloride was decomposed by covering with 100 cc. of benzene and then adding slowly 120 g. of a 16% solution of sodium hydroxide. The benzene solution of the free amino ester was separated and the water layer was extracted with another 100 cc. of benzene. The combined benzene extracts were evaporated and the ester was distilled under reduced pressure. The yield of product, b. p. 101–103° (6 mm.), was 4.3 g. (30% of the theoretical amount). The ester is a colorless, limpid liquid; $n_D^{25} = 1.4643$; $d_4^{25} = 1.0131$; M_D, calcd., 46.98; found, 46.62.

Titration. Subs., 0.1150: 9.45 cc. of $N/14$ HCl. Calcd. for $C_9H_{17}NO_2$: neutral equivalent, 171.1; found: 170.

The chloroplatinate was obtained from the hydrochloride and platinum chloride. It melts at 181° and is moderately soluble in water.

Anal. Subs., 0.0727: Pt, 0.0190. Calcd. for $(C_9H_{17}NO_2)_2.H_2PtCl_6$: Pt, 26.1. Found: Pt, 25.95.

2-β-Piperidylethanol-1.—Eleven and one-half g. of ethyl β-piperidyl acetate was dissolved in 200 cc. of boiling absolute alcohol and 10 g. of sodium was added with stirring. The mixture was refluxed for about one-half hour until the sodium was entirely dissolved and then 25 cc. of water was added. The solution was evaporated under pressure and about 30 cc. of water was added in portions from time to time as solid separated. When the volume was about 50–60 cc. the solution was cooled and extracted about five times with 25cc. portions of ether. The ether was evaporated and the residue distilled under reduced pressure. The yield of product, b. p. 121–123° (6 mm.), was 5.5 g. (63% of the theoretical amount). The amino alcohol is a colorless liquid, somewhat less viscous than 8-piperidyl carbinol; $n_D^{25} = 1.4888$; $d_4^{25} = 1.0106$; M_D, calcd., 37.73; found: 36.85.

Titration. Subs., 0.0923: 10.10 cc. of $N/14$ HCl. Calcd. for $C_7H_{15}ON$, neutral equivalent, 129.1; found: 127.

Anal. Subs., 0.1700: CO_2, 0.4032 g.; H_2O, 0.1774 g. Calcd. for $C_7H_{15}ON$: C, 65.07; H, 11.71. Found: C, 64.8; H, 11.60.

The chloroplatinate and chloro-aurate were not obtained in the crystalline condition.

β-Methylene Piperidine.—Sixty-five g. of phosphorus pentoxide covered with 25 cc. of toluene was placed in a flask in an oil-bath at 125°. A solution of 10.5 g. of β-piperidyl carbinol in 50 cc. of toluene was added and the solvent was allowed to distil. When most of the toluene was removed, the residue was heated to about 180–190" for two hours. The flask was cooled and the contents were treated with about 200 g. of ice. Solid potassium hydroxide was added until the mixture was strongly alkaline and the mixture was steam distilled until 200 cc. of distillate was obtained. The distillate was first extracted with 100 cc. of ether and the water layer was then acidified with hydrochloric acid and evaporated to dryness.

The ether extract was dried over solid potassium hydroxide. Titration of a sample with standard acid indicated a yield of 20% of the desired amine. The hydrochloride was precipitated by passing dry hydrogen chloride into the ether solution. The precipitate was collected on a filter, washed with ethyl acetate and dried over phosphorus pentoxide.

Anal. Subs., 0.1082, 3.56 cc. of 0.2075 N $AgNO_3$. Calcd. for $C_6H_{12}NCl$: Cl, 27.5. Found: Cl, 27.6.

The hydrochloride obtained from the aqueous and ether portions of two such runs was decomposed with 20 g. of 50% potassium hydroxide solution and the free amine boiled at 125–145°, mainly at 138°. Only 0.4 g. was obtained.

Titration. Subs., 0.1910: 26.7 cc. of $N/14$ HCl. Calcd. for $C_6H_{11}N$, neutral equivalent: 97.1; found, 100. The physical constants on this sample were: n_D^{20}, 1.4807; d_4^{20}, 0.9342; M_D, calcd., 31.00; found, 29.85.

β-Vinyl Piperidine.—Using a procedure identical with that described above, 12.4 g. of 2-β-piperidylethanol-1 was dehydrated. The hydrochloride came down as a gummy mass. The yield of free base, b. p. 152–155°, was 1.4 g. (13% of the theoretical amount).

Titration. Subs., 0.0824: 6.41 cc. of 0.1138 N HCl. Calcd. for $C_7H_{13}N$: neutral equivalent, 111.1; found, 113.2.

8-Vinyl piperidine of this purity has the following physical constants: $n_D^{25} = 1.4731$; $d_4^{25} = 0.9274$; M_D, calcd., 35.62; found: 33.61.

The chloroplatinate separated as a gummy solid from water but crystallized from 70% alcohol. The product darkened at 220° and melted with decomposition at 223–224°.

Anal. Subs., 0.1535, 0.0502: Pt, 0.0452, 0.0147. Calcd. for $(C_7H_{13}N)_2.H_2PtCl_6.2H_2O$: Pt, 29.27. Found: Pt, 29.5.

Summary

β-Vinyl piperidine has been prepared from β-piperidyl carbinol and most of the intermediate products have been isolated and characterized.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

FURTHER OBSERVATIONS CONCERNING THE MIGRATION OF ACYL FROM NITROGEN TO OXYGEN

BY L. CHAS. RAIFORD AND F. C. MORTENSEN

RECEIVED DECEMBER 27, 1927 PUBLISHED APRIL 5, 1928

Studies published from this Laboratory[1] have shown that, in general, but one acetyl-benzoyl derivative of an ortho-aminophenol can be obtained, regardless of the order in which the radicals are introduced.[2] When one of the reacting groups (amino and hydroxyl) is on a side chain, as in *o*-hydroxybenzylamine and its isomeride, o-aminobenzyl alcohol, isomeric mixed diacyl derivatives were obtained and no rearrangement was observed.[3] This behavior, as well as the results reported by Auwers and co-workers[4] to the effect that they observed a rearrangement in which acyl wandered from oxygen to nitrogen when oxygen was attached to the ring and nitrogen was on a side chain, raised the question of the extent to which this migration is influenced by the cyclic radical of the starting

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[1] Raiford and Lankelma, THIS JOURNAL, 47,1111 (1925).

[2] For exceptions, see Raiford and Couture, *ibid.*, 46,2307 (1924).

[3] Raiford and Clark, *ibid.*, 45, 1738 (1923).

[4] Auwers and others, Ber., 33,1923 (1900).

material. That the particular structure of the latter cannot be the sole cause of the migration seems probable, for it has been observed in naphthalene[5] as well as in benzene derivatives. Thus **Armstrong**[6] was able to obtain but one acetyl-benzoyl derivative from 1-amino-2-naphthol and its halogenated substitution products, while Raiford and Clark[7] found that acetylation of 8-benzoylamino-1-naphthol and benzoylation of 8-acetylamino-1-naphthol gave but one product, and that this had the benzoyl radical attached to nitrogen.

In the experiments recorded below, one of the bases used was *o*-**amino-cyclohexanol**,[8] which differs from o-aminophenol to the extent that it is a cycloparaffin instead of a benzene derivative. The second was a-amino-benzyl-2-naphthol, m. p. 125°,[9] in which the amino radical was attached to a side chain. Though the acyl radicals were introduced in both possible orders in each instance, no rearrangement was observed.

Experimental Part

A. Derivatives of o-Aminocyclohexanol

2-Benzoylaminocyclohexanol.—This was prepared in **97%** yield by treatment of *o*-**aminocyclohexanol** in caustic alkali solution with **1.5** molecular proportions of **benzoyl** chloride in the usual way. Crystallization from benzene gave nearly colorless, short needles, **m.** p. 168–169°.

Anal. Subs., **0.1372, 0.2011:** CO_2, **0.3583;** H_2O, **0.0923; 9.20** cc. of **0.1** *N* acid. Calcd. for $C_{13}H_{17}O_2N$: C, **71.23;** H, **7.76;** N, **6.39.** Found: 71.20, 7.40, **6.40.**

2-Benzoylaminocyclohexyl Benzoate.---Six g. of the above-described product was dissolved in **25** cc. of pyridine and treated with **1.5** molecular proportions of **benzoyl** chloride as directed by Einhorn and **Hollandt.**[10] A yield of **93%** was obtained. Portions crystallized from benzene and alcohol, respectively, separated in colorless needles, m. p. 204–205°.

Anal. Subs., **0.3211, 0.5002:** CO_2, **0.8637;** H_2O, **0.1897; 15.64 cc.** of **0.1** N acid. Calcd. for $C_{20}H_{21}O_3N$: C, **74.30;** H, **6.50;** N, **4.33.** Found: **73.34, 6.56, 4.37.**

Hydrolysis of the **Dibenzoyl** Derivative.—When **3.5 g.** was warmed with **16** cc. of alcoholic potassium hydroxide containing **1.5** molecular proportions of the alkali, all was dissolved. After thirty minutes the liquid was neutralized with concentrated hydrochloric acid, the potassium chloride filtered off, the filtrate concentrated and allowed to

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[5] It is well known that many naphthalene derivatives show a behavior similar to that of an aliphatic rather than that of a true benzene compound [Graebe, Ber., **13, 1849** (1880); Liebermann and **Hagen,** Ber., **15,1427** (1882)].

[6] Armstrong, unpublished report.

[7] Raiford and Clark, THIS JOURNAL, 48, **483 (1926).**

[8] This product, m. p. 65°, corresponds to that first prepared by **Brunel** [*Compt. rend.*, **137,** 198 (1903)] and recorded by Richter as the *cis* form. Senderens and **Aboulenc** [*ibid.*, **177, 160 (1923)**] obtained by reduction of o-aminophenol, in presence of nickel, what they regarded as a mixture of the *cis* and trans forms. No record of the pure trans form was found.

[9] **Betti** [*Gazz. chim. ital.*, 36, **II, 392 (1906)**] recorded 124° for the **racemic** form.

[10] Einhorn and Hollandt, Ann., 301, **101 (1898).**

stand overnight. The solid deposited represented a yield of **90%.** Crystallization from benzene gave needles, melting at 168–169°, which were identified by mixed melting point as 2-benzoylaminocyclohexanol.

2-Benzoylaminocyclohexyl Acetate.—Ten g. of the *N*-benzoyl derivative was acetylated by Liebermann and Hörmann's[11] method. A yield of 84% was obtained. Crystallization from 50% alcohol gave nearly colorless plates, m. p. 143–144°.

And. Subs., 0.3192, 0.2008: CO_2, 0.8045; H_2O, 0.2087; 7.6 cc. of 0.1 N acid. Calcd. for $C_{15}H_{19}O_3N$: C, 68.96; H, 7.28; N, 5.36. Found: 68.73, 7.26, 5.29.

Hydrolysis of the above-described product caused the loss of the acetyl radical. The N-benzoyl derivative, m. p. 168–169°, was recovered to the extent of 87%.

2-Acetylaminocyclohexyl Acetate.—This product was obtained by heating a mixture of equal weights of the free base and anhydrous sodium acetate with an excess of acetic anhydride for a few minutes. The crystalline mass that formed on cooling was dissolved in water, extracted with ether, the extract dried with anhydrous sodium sulfate and the ether distilled off. The residue was purified by treatment of its benzene solution with ligroin (b. p. 70–80°) which gave irregularly shaped crystalline masses, m. p. 117–118".

Anal. Sub., 0.1941, 0.1999: CO_2, 0.4290; H_2O, 0.1480; 10.09 cc. of 0.1 N acid. Calcd. for $C_{10}H_{17}O_3N$: C, 60.30; H, 8.54; N, 7.03. Found: 60.27, 8.47, 7.06.

The diacetyl derivative was hydrolyzed with alcoholic potassium hydroxide, as indicated above. After neutralization by hydrochloric acid and removal of potassium chloride, the filtrate was concentrated to one-third its volume and allowed to stand. A yield of 81% of the *N*-acetyl derivative separated. Crystallization from benzene gave needles that melted at 314–315° and which were identical with the mono-acetyl compound prepared directly from the free base by Lumière and Barbier's[12] method.

2-Acetylaminocyclohexyl Benzoate.—One g. of the N-acetylaminohexanol dissolved in 10 cc. of water containing 0.4 g. of sodium hydroxide was mixed with 1.5 molecular proportions of benzoyl chloride, the mixture shaken for thirty minutes and allowed to stand for twelve hours; yield, 81%. After recrystallization from benzene, the product melted at 198–199°.

Anal. Subs., 0.3180, 0.2004: CO_2, 0.8022: H_2O, 0.2074; 7.70 cc. of 0.1 N acid. Calcd. for $C_{15}H_{19}O_3N$: C, 68.96; H, 7.27; N, 5.36. Found: 68.79, 7.24, 5.38.

This diacyl derivative was hydrolyzed with alcoholic potassium hydroxide as described above and the filtrate left after removal of potassium chloride was evaporated until crystals appeared. Recrystallization from benzene gave needles that melted at 313–315° and which were identified as 2-acetylaminocyclohexanol.

B. Derivatives of α-Aminobenzyl-2-naphthol

a-Acetylaminobenzyl-2-naphthyl Benzoate.—One g. of a-acetylaminobenzyl-2-naphthol,[13] m. p. 240–241°, dissolved in pyridine, was treated with excess of benzoyl chloride as directed by Einhorn and Hollandt.[14] A yield of 75% was obtained. Crystallization from alcohol gave nearly colorless needles, m. p. 176–177".

Anal. Subs., 0.1010: 2.57 cc. of 0.1 N acid. Calcd. for $C_{26}H_{21}O_3N$: N, 3.54. Found: 3.56.

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[11] Liebermann and Hormann, *Ber.*, **11**, 1619 (1878).

[12] Lumière and Barbier, *Bull. soc. chim.*, **33**, 784 (1905).

[13] This material was obtained by following the series of preparations described by Betti, *Gazz. chim. ital.*, **33**, *I*, 7 (1903), who recorded 236–237° as the melting point.

[14] Einhorn and Hollandt, *Ann.*, **301**, 95 (1898). The Schotten-Baumann method was not successful in this case.

Hydrolysis of the above product gave the *N*-acetyl naphthol from which the diacyl derivative was prepared.

α-Benzoylaminobenzyl-2-naphthyl Benzoate.—This product was obtained in 96% yield from the corresponding aminonaphthol by the Schotten-Baumann method when an excess (4 molecular proportions) of benzoyl chloride was used. Crystallization from benzene gave fawn-colored nodules, m. p. 118–119".

Anal. Subs., 0.2012: 4.42 cc. of 0.1 N acid. Calcd. for $C_{31}H_{23}O_3N$: N, 3.06. Found: 3.07.

Hydrolysis of the dibenzoyl derivative gave an almost quantitative yield of a phenolic product which, after crystallization from alcohol, melted at 240–241°.[15] The same product was obtained in the present work by benzoylation of the hydrochloride of the corresponding aminonaphthol with 2 molecular proportions of benzoyl chloride. Analysis indicated a monobenzoyl derivative.

Anal. Subs., 0.2005: 5.72 cc. of 0.1 *N* acid. Calcd. for $C_{24}H_{19}O_2N$: N, 3.96. Found: 3.99.

α-Benzoylaminobenzyl-2-naphthyl Acetate.—Ten g. of the corresponding N-benzoylaminonaphthol and an equal weight of anhydrous sodium acetate were warmed for ten minutes with 25 cc. of acetic anhydride. Water was added to the cold mixture and the solution extracted with ether. The residue after distillation of the ether was purified by pouring its alcoholic solution into water with rapid stirring. Nearly colorless needles separated; yield, 90%; m. p. 118–119°.

Anal. Subs., 0.5027: 12.47 cc. of 0.1 N acid. Calcd. for $C_{26}H_{21}O_3N$: N, 3.54. Found: 3.47.

Hydrolysis of this product gave the benzoylaminonaphthol from which the diacyl derivative was obtained.

Summary

1. The acetyl-benzoyl derivatives of o-aniinocyclohexanol were obtained in isomeric forms that showed no tendency to rearrange.

2. The observations made with mixed diacyl derivatives of α-aminobenzyl-2-naphthol indicate that the migration characteristic of ortho-aminophenols does not occur when one of the reacting groups is attached to a side chain. This confirms the conclusions previously reached.

IOWA CITY, IOWA

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[15] Betti (ref. 13) recorded 224° for a compound obtained by action of benzoyl chloride on the benzylaminonaphthol, and which analyzed for *a* monobenzoyl derivative. A mixture of our product and a-acetylaminobenzyl-2-naphthol, m. p. 240–241°, melted at 218–223°.

[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

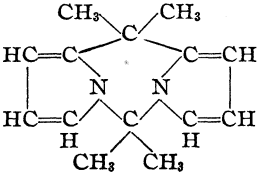
THE MOLECULAR SYMMETRY OF ACETONYL PYRROLE

BY STERLING B. HENDRICKS

RECEIVED DECEMBER 27, 1927 PUBLISHED APRIL 5, 1928

The x-ray diffraction patterns obtained from complicated organic compounds have been interpreted in several different ways. The determination of the smallest unit of structure by the use of Laue and spectrum photographs is the only one of these methods not involving questionable assumptions. As a rule a complete structure determination cannot be made but, in most cases, the minimum symmetry of the molecule can be determined. The fixing of this minimum symmetry is of great value in the study of the geometrical configurations of organic compounds.

Acetonyl pyrrole is a condensation product of acetone and pyrrole.[1] C. Liebermann and R. Kraus assigned it the following formula



Condensation supposedly takes place between two moles of acetone and two of pyrrole with the elimination of water, the hydrogen atoms being removed from the N and the *a*-C atoms. It has been described[2] as crystallizing in the tetragonal system with $a:c = 1:0.8343$.

The material used in this investigation was prepared by heating 10 g. of pyrrole (Eastman) with 15 g. of acetone in 300 cc. of 90% ethyl alcohol containing 4 cc. of concentrated hydrochloric acid.' The crystalline material was separated and recrystallized several times from acetone. Crystals several millimeters in length were obtained by crystallization from acetone solutions containing small amounts of benzene. The developed crystals were elongated octahedra showing evident pyramidal character.

Laue photographs were made with the incident x-ray beam normal to (100) and making small angles with this normal. Data obtained from one of these photographs are listed in Table I. Spectrum photographs were made on which (100) and (001) reflected as the principal spectrum. These faces were initially parallel to the x-ray beam and were oscillated through an angle of 20° with first the c- and then the b-axis in the axis of rotation in the former case and the b-axis in the latter case. It was very difficult to obtain accurate spacing measurements for d_{100} since

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[1] (a) Baeyer, *Ber.*, 19,2184 (1886); (b) Dennstedt and Zimmerman, *ibid.*, 20,2450 (1887); (c) C. Liebermann and R. Kraus, *ibid.*, 40,2504 (1907).

[2] Fock, *Z. Krist*, 14, 541 (1888).

TABLE I

TYPICAL LAUE PHOTOGRAPHIC DATA FROM ACETONYL PYRROLE

The incident x-ray beam was approximately normal to (100)

Plane	d_{hkl}, Å.	$n\lambda$	Intensity	Plane	d_{hkl}, Å.	$n\lambda$	Intensity
$1\bar{6}0$[a]	1.659	0.48	v.w.	1.4.13	1.465	0.45	v.w.
162	1.643	.46	v.w.	$2\bar{9}0$	1.094	.42	v.w.
162	1.643	.38	w.	$2\bar{9}4$	1.076	.41	v.w.
$1.\bar{1}.15$	1.548	.46	v.w.	1.3.15[b]	1.431	.43	v.w.
166	1.530	.35	w.	1 . 3	1.499	.47	v.w.
1.3.14	1.499	.45	v.w.	1.4.14	1.395	.45	v.w.

[a] The indices used in this publication are referred to the space group axes

[b] Data from a second photograph.

it was impossible to determine whether or not reflections from (100) were present. The data listed for (100) in Table II were obtained by measurements to the mid-point of the zone for which h is a constant. In these photographs (100) reflected as the principal spectrum and the crystal, with its b-axis in the axis of rotation, was oscillated through an angle of 20°. Spacing measurements were made on reflections from (001), sodium chloride being used as a reference substance (transmission). The spacing d_{001}/n obtained from these measurements is 5.975 Å. in agreement with the value 5.950 Å. calculated from d_{100}/n = 10.09 Å. and the observed axial ratio. The smallest unit of structure compatible with the Laue and spectrum data has $a_0 = b_0 =$ 10.09 Å., $c_0 =$ 23.85 Å. The density calculated on the basis of this unit containing 8 $C_{14}H_{18}N_2$ is 1.132 in agreement with the density 1.162 determined by the Retgers suspension method.

TABLE II

TYPICAL SPECTRUM PHOTOGRAPHIC DATA FROM ACETONYL PYRROLE, MO K RADIATION

Plane	Line	Order	d_{hkl}, Å.	Intensity[a]
001	MoKβ	4	...	s.
	α_1	4	24.30	v.s.
	α_1	8	...	abs.
	α_1	12	23.72	m.
	α_1	16	...	v.w.
100	α_1	2	10.48	
	α_1	3	10.10	
	α_1	4	10.12	
	α_1	5	10.19	

[a] The following abbreviations are used throughout this paper: v.s., very strong; s., strong; m.s., medium strong; m., medium; m.w., medium weak; w., weak; v.w., very weak.

The observation that a Laue photograph made with the incident x-ray beam normal to (100) shows only a horizontal plane of symmetry requires the structure to be isomorphous with one of the point groups 4*c*, 4C or 4*Ci*. Reflections were obtained in the first order from planes having

$(h + k + l)$ both odd and even. The underlying lattice is therefore the simple tetragonal one.

The most characteristic feature of the spectrum photographs was the presence of reflections from (001) in only the 4th, 8th, etc., orders (Fig. 1). The only space groups based upon a simple tetragonal lattice and having the symmetry of one of the point groups $4c$, 4C or 4Ci explaining this observation are 4C-2 and 4C-4. The possible molecular centers in these two cases[3] are

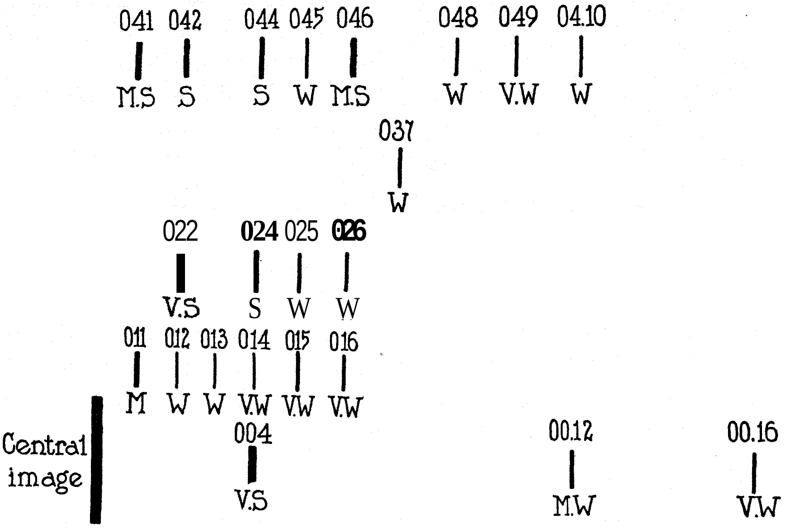

Fig. 1.—A reproduction of a spectrum photograph showing reflection from (001) in the equatorial zone. The b-axis of the crystal was vertical. Only the Mo Ka lines are shown; 20° oscillation.

$$\text{4C-2}\quad (a)\quad xyz;\ \bar{y},x,z+\tfrac{1}{4};\ \bar{x},\bar{y},z+\tfrac{1}{2};\ y,\bar{x},z+\tfrac{3}{4}$$
$$\text{4C-4}\quad (a)\quad xyz;\ \bar{y},x,z+\tfrac{3}{4};\ \bar{x},\bar{y},z+\tfrac{1}{2};\ y,\bar{x},z+\tfrac{1}{4}$$

In either case there can be only four equivalent molecules in the unit of structure. It is thus possible that if $C_{14}H_{18}N_2$ is the structural molecule there are two sets of such molecules. It is more probable, however, that the real structural molecule is $C_{28}H_{36}N_4$ corresponding to a condensation product of four moles of pyrrole with four of acetone.

An investigation of the literature showed that the original formula had been assigned without a molecular weight determination being made. For this reason it was necessary to make such a determination. The previously described differential vapor pressure method[4] was used, benzene

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[3] **R. W. G. Wyckoff, "An Analytical Expression of the Results of the Theory of Space Groups,"** ***Carnegie Inst. Pub.***, **No. 318, Washington, 1922, p. 80.**

[4] **Menzies, THIS JOURNAL, 43, 2309–2314 (1921); Menzies and Wright,** ***ibid.***, **43, 2314–2323 (1921).**

being used as the solvent; 0.656 g. of acetonyl pyrrole in 100 cc. of the solvent at the boiling point gave an equivalent boiling point elevation of 0.052°, corresponding to a molecular weight of 403. The molecular weight calculated for $C_{28}H_{36}N_4$ is 428. It thus seems very probable that $C_{28}H_{36}N_4$ is the structural molecule. These molecules, since their centers are in the general positions, do not necessarily have an element of symmetry.

The formula $C_{28}H_{36}N_4$ depends upon the analysis of Dennstedt and Zimmerman.[1] It is possible that the hydrogen content of the molecule is not correctly given. Such a possibility does not influence the correctness of the above conclusions concerning the molecular symmetry and the number of molecules associated with the unit of structure.

Summary

Laue and spectrum photographs have been obtained and analyzed from crystals of acetonyl pyrrole. The unit of structure containing four $C_{28}H_{36}N_4$ molecules has the dimensions $a_0 = b_0 = 10.09$ Å., $c_0 = 23.85$ Å. The space group is 4C-2 or 4C-4, the molecules being in the general positions and thus not necessarily having an element of symmetry. The molecular weight is twice that corresponding to the previously assigned formula. A determination of the molecular weight by a differential vapor pressure method gave a value in agreement with the formula $C_{28}H_{36}N_4$.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

PHENYLETHYLMALONIC METHYL ESTER. A NEW METHOD OF SYNTHESIS

BY MARY M. RISING AND TSOH-WU ZEE[1]

RECEIVED DECEMBER 27, 1927 PUBLISHED APRIL 5, 1928

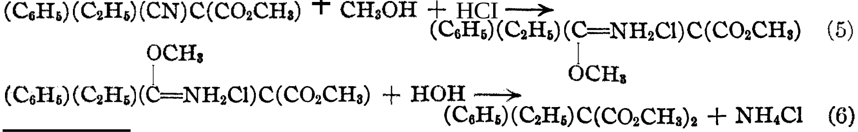
There appeared recently a paper[2] in which there was described a method of preparation of phenylethylmalonic methyl ester, $(C_6H_5)(C_2H_5)C(CO_2CH_3)_2$, by a procedure summarized as follows.

$$(C_6H_5)CH_2(CN) + NH_2Na + C_2H_5I \longrightarrow (C_6H_5)(C_2H_5)CH(CN) + NaI + NH_3\uparrow \quad (1)$$

$$2(C_6H_5)(C_2H_5)CH(CN) + 2Na \longrightarrow 2(C_6H_5)(C_2H_5)C{=}C{=}NNa + H_2\uparrow \quad (2)$$

$$(C_6H_5)(C_2H_5)C{=}C{=}NNa \rightleftarrows (C_6H_5)(C_2H_5)(CN)CNa \quad (3)$$

$$(C_6H_5)(C_2H_5)(CN)CNa + ClCO_2CH_3 \longrightarrow (C_6H_5)(C_2H_5)(CN)C(CO_2CH_3) + NaCl \quad (4)$$



$$(C_6H_5)(C_2H_5)(CN)C(CO_2CH_3) + CH_3OH + HCl \longrightarrow (C_6H_5)(C_2H_5)(\underset{\substack{|\\ OCH_3}}{C}{=}NH_2Cl)C(CO_2CH_3) \quad (5)$$

$$(C_6H_5)(C_2H_5)(\overset{\substack{OCH_3\\ |}}{C}{=}NH_2Cl)C(CO_2CH_3) + HOH \longrightarrow (C_6H_5)(C_2H_5)C(CO_2CH_3)_2 + NH_4Cl \quad (6)$$

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[1] This paper describes work done by Tsoh-Wu Zee in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago, 1926.

[2] Rising and Zee, THIS JOURNAL, 49, 541 (1927).

The ester is an intermediate product in the synthesis of the hypnotic phenylethylbarbituric acid, or pheno-barbital, $(C_6H_5)(C_2H_5)\text{-}\underline{\text{CCONHCONHCO}}$, a valuable therapeutic agent in the treatment of epilepsy, and is therefore a compound of considerable importance. It was first prepared in this Laboratory in 1918 in the course of the synthesis of pheno-barbital,[3] undertaken as a war measure. Condensation of phenylethylmalonic methyl ester with urea produced phenylethylbarbituric acid.

$$(C_6H_5)(C_2H_5)C(CO_2CH_3)_2 + (NH_2)_2CO \longrightarrow (C_6H_5)(C_2H_5)\underline{\text{CCONHCONHCO}} + 2CH_3OH \quad (7)$$

Other methods of production of phenylethylmalonic methyl ester have been sought more recently in the hope of improving the yield of ester obtained in the earlier synthesis (76% of crude material). As the plan of preparation developed during the war constitutes the basis for the commercial production of pheno-barbital, the importance of obtaining good yields is apparent. The first of the recent methods[2] is particularly interesting and valuable for its discovery of a series of sodium salts of aromatic nitriles;[4] it is not as satisfactory from the point of view of yield as is the plan outlined in the present paper.

Another method of synthesis of phenylethylmalonic methyl ester is now to be reported in which the yield of ester is the best so far obtained by any process. This plan makes use of the following reactions.

$$(C_6H_5)CH_2(CN) + NH_2Na + C_2H_5I \longrightarrow (C_6H_5)(C_2H_5)CH(CN) + NaI + NH_3\uparrow \quad (8)$$

$$(C_6H_5)(C_2H_5)CH(CN) + CH_3OH + HCl \longrightarrow (C_6H_5)(C_2H_5)CHC({=}NH_2Cl)(OCH_3) \quad (9)$$

$$(C_6H_5)(C_2H_5)CHC({=}NH_2Cl)(OCH_3) + HOH \longrightarrow (C_6H_5)(C_2H_5)CH(CO_2CH_3) + NH_4Cl \quad (10)$$

$$2(C_6H_5)(C_2H_5)CH(CO_2CH_3) + 2Na \longrightarrow 2(C_6H_5)(C_2H_5)C{=}C(OCH_3)(ONa) + H_2\uparrow \quad (11)$$

$$(C_6H_5)(C_2H_5)C{=}C(OCH_3)(ONa) \rightleftarrows (C_6H_5)(C_2H_5)C(CO_2CH_3)Na \quad (12)$$

$$(C_6H_5)(C_2H_5)C(CO_2CH_3)Na + ClCO_2CH_3 \longrightarrow (C_6H_5)(C_2H_5)C(CO_2CH_3)_2 + NaCl \quad (13)$$

The total yield of phenylethylnialonic methyl ester obtained by this method, calculated from the amount of phenylacetonitrile used, was 43.1%, as compared with 27.4% by the first method of Zee and 41.0% in the war-time synthesis.

Of particular interest in the series of reactions just enumerated is that represented by Equation 11. a-Sodium-a-phenylbutyric methyl ester is produced by treatment of a-phenylbutyric methyl ester with sodium in dry ether. The sodium salt is a white, amorphous substance of interesting

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[3] Rising and Stieglitz, THIS JOURNAL, 40,725 (1918).

[4] A paper entitled "Sodium Salts of Aromatic Nitriles," by Rising and Zee will be published shortly in THIS JOURNAL.

behavior. It takes part in substitution reactions, the group entering the molecule becoming attached to the carbon atom carrying the phenyl group. For example, when treated with chloroformic ester the carbmethoxy group, —$COOCH_3$, replaces the sodium atom, and the salt is converted into phenylethylmalonic methyl ester, as shown in reaction 13. This behavior indicates that the salt is a carbide of structure $(C_6H_5)(C_2H_5)C(CO_2CH_3)Na$. The carbide is undoubtedly a tautomer of an enol salt of structure $(C_6H_5)(C_2H_5)C{=}C(OCH_3)(ONa)$, and the latter is analogous to enol sodium acetoacetic ester, $CH_3COCH{=}C(OC_2H_5)(ONa)$. It is probable that enol a-sodium a-phenylbutyric methyl ester is formed by the reaction of a-phenylbutyric methyl ester with sodium, and that under the conditions used for the conversion of the salt into phenylethylmalonic ester, tautomerization of the enol salt to the more reactive carbide occurs, this being the reactive molecule in substitutions. A detailed formulation of these changes follows.

$$[(C_6H_5)(C_2H_5)C^-(CO_2CH_3)]H \leftrightarrows [(C_6H_5)(C_2H_5)C{=}C(OCH_3)O^-]H \qquad (14)$$

Keto a-phenylbutyric methyl ester Enol a-phenylbutyric methyl ester

$$2[(C_6H_5)(C_2H_5)C{=}C(OCH_3)O^-]H + 2Na \longrightarrow 2[(C_6H_5)(C_2H_5){=}C(OCH_3)O^-]Na + H_2\uparrow \qquad (15)$$

The negative enol ion of the salt tautomerizes to the carbide ion

$$[(C_6H_5)(C_2H_5){=}C(OCH_3)O^-]Na \leftrightarrows [(C_6H_5)(C_2H_5)C^-(CO_2CH_3)]Na \qquad (16)$$

$$[(C_6H_5)(C_2H_5)C^-(CO_2CH_3)]Na + ClCO_2CH_3 \longrightarrow (C_6H_5)(C_2H_5)C(CO_2CH_3)_2 + NaCl \qquad (17)$$

a-Sodium a-phenylbutyric methyl ester is decomposed by water and all acids into a-phenylbutyric methyl ester. The reaction may occur as follows.

$$[(C_6H_5)(C_2H_5)C{=}C(OCH_3)O^-]Na + H_2SO_4 \longrightarrow [(C_6H_5)(C_2H_5)C{=}C(OCH_3)O-]H + NaHSO_4 \qquad (18)$$

$$[(C_6H_5)(C_2H_5)C{=}C(OCH_3)O^-]H \rightleftarrows [(C_6H_5)(C_2H_5)C^-(CO_2CH_3)_2]H \qquad (19)$$

Experimental Part

1. a-Phenylbutyronitrile, $(C_6H_5)(C_2H_5)CH(CN)$.—α-Phenylbutyronitrile was prepared according to the method of Bodroux and Taboury.[5] Experience has taught us that the most satisfactory results, both in yield and purity of product, are obtained only when certain precautions are observed: the purest phenylacetonitrile and sodamide (Kahlbaum's) were used; all apparatus and reagents were thoroughly dried; several fractionations of the product of the reaction were made in *vacuo*. These details are fully discussed in a previous paper.[2] Under the conditions described therein yields as high as 87.4% were obtained of pure a-phenylbutyronitrile of boiling point 114–115° (uncorr.) at 16 mm. Equations 8–13, expressing this reaction and those to be described subsequently, are to be found in the introduction.

2. a-Phenylbutric **Methylimino** Ester Hydrochloride, $(C_6H_5)(C_2H_5)CHC(:NH_2Cl)(OCH_3)$.—In general the procedure developed by Stieglitz and Carr[6] for the

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[5] Bodroux and Taboury, Bull. *soc. chim.*, [7] 4,666 (1910).

[6] Carr, unpublished Doctor's Dissertation, University of Chicago, 1910.

preparation of imino ester hydrochlorides was followed. a-Phenylbutyronitrile was converted into its methyl imino ester hydrochloride by treatment of the nitrile with absolute methyl alcohol and hydrogen chloride in dry ether. It is of the utmost importance that all apparatus and reagents used should be thoroughly dry. The reaction vessel was fitted with a two-holed stopper holding an inlet and an outlet tube, the latter protected from moisture by means of a large calcium chloride tube. Nitrile (I mole) and absolute methyl alcohol ($1^1/_4$ moles) were introduced into this vessel through a pipet inserted into the outlet tube. Two volumes of ether were siphoned into the vessel through the outlet tube from the container in which it was kept in quantity over bright sodium. Hydrogen chloride, dried by being led first through concentrated sulfuric acid and then over phosphorus pentoxide, was brought into the reaction mixture in a rapid stream until the solution was saturated, the temperature of the mixture being kept at $-5°$ to $-10°$ during the passage of the gas. When saturation was complete the flow of gas was interrupted, the inlet tube of the reaction vessel was tightly plugged, and the reaction mixture was allowed to stand for two hours at $-10°$. At the end of this time the stopper was removed from the reaction vessel; the vessel was brought into a vacuum desiccator which was charged with soda lime and phosphorus pentoxide and the desiccator placed in a refrigerator overnight without evacuation. The next day the desiccator was brought over a suction pump for an hour to remove the excess of methyl alcohol, as well as ether. The reaction vessel was then removed from the desiccator, 200 cc. of dry ether was introduced into the vessel and it was quickly closed by means of a piece of rubber dam tied tightly over the opening, a stirring rod being inserted in the rubber. When the contents of the tube were stirred, white, granular crystals formed. These were washed with a mixture of dry ether and dry benzene (1:1), the wash solution being siphoned into and out of the reaction vessel. The crystals were then placed in a desiccator over soda lime and phosphorus pentoxide. They showed a melting point of 92°, and decomposed slightly on standing. Their purity was shown by analysis.

Anal. Subs., 0.1200, 0.1244: 5.64, 5.82 cc. of 0.1 *N* $AgNO_3$; factor, 0.9923. Calcd, for $C_{11}H_{16}NOCl$: Cl, 16.60. Found: 16.53, 16.45.

The yield of hydrochloride from 26.5 g. of nitrile was 30 g., or 76.9%.

3. a-Phenylbutyric Methyl Ester, $(C_6H_5)(C_2H_5)CH(CO_2CH_3)$.—**α-Phenylbutyric** methyl ester was obtained by the hydrolysis of a-phenylbutyric methyl imino ester hydrochloride. For this purpose the hydrochloride (20 g.) was dissolved in 100 cc. of water at 40°, whereupon the solution clouded due to the formation of a-phenylbutyric methyl ester. The temperature of 40° was maintained for ten minutes and the solution was then cooled and extracted with ether, the ether layer being decanted from the water, which was again warmed, cooled and extracted with ether. The ether extracts were combined, dried over fused calcium chloride, and the ether was removed by distillation. The oil which remained was distilled, boiling at 225–226° (uncorr.). When allowed to stand for a time in a desiccator this oil solidified and the white, transparent needles which formed melted at 77–78". Neure,[7] who first prepared the ester, states that it is an oil of boiling point 228°; our product was evidently purer than his. The ester was identified by its hydrolysis products, a-phenylbutyric acid of melting point 43°, and methyl alcohol, and by analysis.

Anal. Subs., 0.1161: CO_2, 0.3161; H_2O, 0.0845. Calcd. for $C_{11}H_{14}O_2$: C, 74.11; H, 7.92. Found: C, 74 24; H, 8.09.

The yield of ester obtained by hydrolysis of the hydrochloride (20 g.) was 15 g. or 90.3%.

4. **a-Sodium-a-phenylbutyric** Methyl Ester, $(C_6H_5)(C_2H_5)C:C(OCH_3)(ONa)$.—

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[7] Neure, *Ann.*, 250, 155 (1889).

a-Sodium-a-phenylbutyric methyl ester was prepared by the treatment of α-phenylbutyric methyl ester with sodium in dry ether. The apparatus and reagents used were carefully dried. The sodium was used in the form of minute globules, prepared by a method outlined in a previous paper.[2] Sodium (1.5 g.) was prepared for use in this way in a flask fitted with a stopper carrying a dropping funnel and a reflux condenser holding at the top a calcium chloride tube. Sodium-dried ether (100 cc.) was then siphoned into the flask through the dropping funnel and 12.8 g of a-phenylbutyric methyl ester (10% in excess of the calculated amount) dissolved in ether was dropped rather slowly into the flask. Shortly a pure white, amorphous precipitate formed, hydrogen was evolved and the ether boiled. The flask and contents were shaken frequently. The sodium was practically all consumed in two hours. The reaction mixture was allowed to stand overnight and was then refluxed for an hour over a water-bath. By this time large quantities of the white precipitate had formed. The supernatant solution was decanted from it and the precipitate was washed several times by decantation with dry ether, care being used to protect it from moisture and carbon dioxide. The salt was then brought onto a Biichner funnel and washed briefly with dry ether, while suction was applied, then removed quickly to a vacuum desiccator. Analysis for sodium showed the salt to be pure.

Anal. Subs., 0.1080, 0.0846: Na_2SO_4, 0.0375, 0.0294. Calcd. for $C_{11}H_{13}O_2Na$: Na, 11.49. Found: 11.23. 11.24.

The yield of the salt from 1.5 g. of sodium and 12.8 g. of a-phenylbutyric methyl ester was 11 g., or 86.9%, calculated in terms of the sodium used. To obtain the salt in pure form it was found necessary to use an excess (about 10%) of a-phenylbutyric methyl ester, so that the last traces of sodium would react, contamination of the salt with particles of the metal being thus avoided. The excess of ester used was readily recovered from the ether filtrate.

a-Sodium-a-phenylbutyric methyl ester is decomposed by water and all acids into a-phenylbutyric methyl ester. Treatment of the salt with cold 50% sulfuric acid produces this ester in 85% yield.

5. Phenylethylmalonic Methyl Ester, $(C_6H_5)(C_2H_5)C(CO_2CH_3)_2$.—Phenylethylmalonic methyl ester was prepared by the treatment of a-sodium-a-phenylbutyric methyl ester with chloroformic ester in ether. All apparatus and reagents were thoroughly dried before use, a-Sodium-a-phenylbutyric methyl ester (10 g.) was suspended in 100 cc. of dry ether. The reaction flask was then closed with a stopper carrying a dropping funnel and a reflux condenser protected at the top by a calcium chloride tube. Chloroformic methyl ester (1.5 g.) was dropped slowly into the flask, whereupon a vigorous reaction occurred, the ether boiled, and a granular precipitate of sodium chloride appeared. When all the chloroformic ester had been added the reaction mixture was heated for an hour over the water-bath and then allowed to stand overnight. The next day small portions of water were added to dissolve the sodium chloride. The ether layer was decanted, the water solution remaining was extracted several times with ether, and these ether extracts were combined with the main ether solution, the whole being dried over granulated calcium chloride. The ether was removed by distillation and the oil remaining crystallized upon cooling into thick, white plates which showed a melting point of 39–40°, the melting point of phenylethylmalonic methyl ester.[8] A mixture of equal quantities of this product and phenylethylmalonic ester of known purity also melted at 39–40°. The yield of ester from 10 g. of the sodium salt was 10 g., or **84.7%.**

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[8] Ref. 3, p. 730; Rising and Zee (ref. *2)* obtained the ester in slightly purer form, melting at 39–40°.

Summary

1. A new method of synthesis of phenylethylmalonic methyl ester, an intermediate in the production of pheno-barbital, is described.

2. The yields at all stages of the process are good and the method is the most satisfactory of all those known at present.

3. The isolation of the salt, a-sodium-a-phenylbutyric methyl ester, an intermediate product in this synthesis, is discussed. The behavior of the salt indicates that it exists in tautomeric forms, of structures $[(C_6H_5)(C_2H_5)C{=}C(OCH_3)O^-]Na^+$ and $[(C_6H_5)(C_2H_5)C^-(CO_2CH_3)]Na^+$.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A NEW MICRO PHOSPHORUS DETERMINATION

BY ADALBERT ELEK

RECEIVED JANUARY 25, 1928 PUBLISHED APRIL 5, 1928

Various methods for the micro determination of phosphorus in organic substances have been described. In most cases, however, the methods used lack either simplicity or accuracy.

The procedure as described by Lieb,[1] though accurate, is inconvenient inasmuch as it involves washing the combustion tube and boiling the boat in dilute nitric acid. The method described by Lieb and Wintersteiner[2] and by Josephson and Sjörberg[3] was found to yield low results for at least one substance, namely, for thymus nucleic acid.

The new method described in this paper eliminates the undesirable features of the methods cited.

Experimental Part

A sample of 3–6 mg. is weighed by difference into a silver crucible of approximately 18 mm. lower diameter, 33 mm. upper diameter and 40 mm. in height. About 0.2 g. of potassium nitrate and 1 g. of potassium hydroxide are then added and the mixture is fused by heating the upper part of the crucible over a small flame with a slow, rotating motion to prevent spattering. In the course of about two to three minutes the fusion is complete, as shown by the clearness of the melt. The crucible is covered and allowed to cool on a copper block. The cooling requires about four minutes. A slight pressure on the walls of the crucible loosens the cake, which is then easily transferred into a large Pyrex test-tube of about 30 mm. diameter and 200 mm. in length. The crucible is then washed 2–3 times with a small quantity of water and the washings are transferred to the test-tube. Enough nitric acid (prepared according to Lieb)[1] is then added to make the volume up to 15 cc. The solution is placed in a boiling water-bath for about ten to fifteen minutes. In some cases the solution is slightly turbid, but on warming in

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[1] Pregl, "Die quantitative organische Mikroanalyse," 2nd ed., Springer (Berlin), 1923, p. 151.

[2] Lieb and Wintersteiner, *Mikrochemie*, 2, 78 (1924).

[3] Josephson and Sjörberg, *Svensk Kemisk Tidskrift*, 36, 267 (1924).

the water-bath the turbidity disappears. Fifteen cc. of molybdate solution (prepared according to Lieb)[1] is then added. The mixture is stirred for about thirty seconds, allowed to stand for a few minutes and then stirred again for a few seconds. The test-tube is covered and allowed to stand for two hours at most, after which time all of the precipitate collects in compact form at the bottom of the test-tube.

The filtration, washing, drying and weighing are carried out as described by Lieb.[1]

Some of the results obtained with pure compounds by this method are given below (Table I).

TABLE I

RESULTS WITH PURE COMPOUNDS

	Subs., mg.	Ammonium phosphomolybdate, mg.	P, calcd., %	P, found, %
Uridine phosphoric acid	3.920	26.345	9.58	9.76
Cytidine phosphoric acid	3.102	20.390	9.61	9.54
Guanylic acid + $2H_2O$	2.960	15.845	7.76	7.77
Adenylic acid + H_2O	4.820	28.265	8.49	8.51
Thymus nucleic acid (Sample I)	2.943	17.490	8.67	8.63
Thymus nucleic acid (Sample II)	3.616	21.329	8.67	8.56

Summary

A new micro method for the determination of phosphorus is described. The analysis is carried out with 3–6 mg. of substance. Data are given for the analysis of some nucleic acid derivatives.

NEW YORK CITY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE IDENTIFICATION OF ORGANOMAGNESIUM HALIDES BY CRYSTALLINE DERIVATIVES PREPARED FROM a-NAPHTHYL ISOCYANATE

BY HENRY GILMAN AND MARGARET FURRY

RECEIVED JANUARY 26, 1928 PUBLISHED APRIL 5, 1928

Introduction

Organomagnesium halides and other reactive organometallic compounds may be conveniently detected, qualitatively, by the sensitive color test described by Gilman and Schulze.[1] Frequently, however, a need is felt for some reagent that will give a solid derivative characteristic of a given RMgX compound. One of the best compounds for this purpose is phenyl isocyanate, because of its smooth reaction at low temperatures to give anilides. This reaction was first investigated by Blaise,[2] and was later[3]

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[1] Gilman and Schulze, THIS JOURNAL, 47, **2002 (1925)**; also, **Bull.** *soc. chim.*, **41, 1479 (1927).**

[2] **Blaise,** *Compt.* **rend.,** 132, **38 (1901).** Also, Gilman and Kinney, THIS JOURNAL, **46,** 493 (1924), for the mechanism of reaction. Others have used phenyl isocyanate in studies on Organomagnesium halides. Recently, Johnson and McEwen, THIS JOURNAL, **48,** 474 (1926), used it for the identification of phenylacetenylmagnesium bromide.

[3] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45,** 150 **(1923).**

tried as one of several methods for the quantitative estimation of Grignard reagents. It has been used in connection with the identification of the —NMgX,[4] and —OMgX[5] and —SMgX[6] groups, and for the preparation of derivatives from organocalcium iodides,? organobarium iodides,[8] organoberyllium halides[9] and beryllium dialkyls.[10]

a-Naphthyl isocyanate is generally available and enjoys some advantages over phenyl isocyanate for the identification of various organometallic compounds. Its greater molecular weight gives amides that are generally less soluble, better crystallized and higher melting than the corresponding anilides obtained when phenyl isocyanate is used. Furthermore, should an excess of a-naphthyl isocyanate be used, which might often be the case when a derivative is prepared from a very small quantity of organometallic compound, the *sym.*-di-α-naphthyl urea (formed subsequent to hydrolysis) is so sparingly soluble in the commoner solvents, particularly petroleum ether, that the separation and purification of the a-naphthalide are made easier than would be the case if phenyl isocyanate were used. a-Naphthyl isocyanate has recently been used for the identification of beryllium dimethyl.[10] Phenyl isocyanate may be preferred to a-naphthyl isocyanate in some cases where the organometallic compounds are not very reactive.[7,8,9] Phenylcarbamine chloride ($C_6H_5NHCOCl$) and phenylcarbamine bromide are more reactive than phenyl isocyanate,[5] from which compound they may very conveniently be prepared.

The present study reports a number of a-naphthalides prepared from typical Grignard reagents. The reaction is very probably applicable to all RMgX compounds, and inasmuch as it is possible to bring so many halides, alkyl and aryl, into reaction with magnesium, the formation of amides should lend itself to the identification of such halides and the compounds from which the halides are prepared. Marvel, Gauerke and Hill[11] have reported on the use of the Grignard reagent for the identification of primary alkyl bromides and iodides by conversion to the corresponding mercuric halides and Hill[12] has just extended this method to the identification of secondary alkyl and aryl bromides and iodides.

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[4] Gilman and Pickens, THIS JOURNAL, 47,2406 (1925).

[5] Gilman and Schulze, *Rec.* trav. *chim.*, 47 (1928). This paper describes a wide variety of reagents used in studies concerned with the characterization of the —OMgX group. The same reagents can, of course, be used for the identification of organometallic compounds where the metal is attached to carbon.

[6] Gilman and King, THIS JOURNAL, 47, 1136 (1925).

[7] Gilman and Schulze, *ibid.*, 48,2463 (1926).

[8] Gilman and Schulze, Bull. *soc. chim.*, 41, 1333 (1927).

[9] Gilman and Schulze, THIS JOURNAL, 49,2904 (1927).

[10] Gilman and Schulze, J. *Chem. Soc.*, 131,2663 (1927).

[11] Marvel, Gauerke and Hill, THIS JOURNAL, 47,3009 (1925).

[12] Hill, *ibid.*, 50, 167 (1928).

Experimental

When an ethereal solution of α-naphthyl isocyanate is added to the Grignard reagent in ether, a smooth reaction takes place and is completed with the addition of the isocyanate. The ethereal solution obtained subsequent to hydrolysis contains the naphthalide. Frequently some *sym.*-di-α-naphthyl urea can be separated by filtration of the solid present at the ether–water interface. The a-naphthalides were purified by crystallization from ethyl alcohol. The process of purification can be considerably simplified by using an excess of Grignard reagent, for in this way, providing proper precautions have been taken to exclude moisture, there should be no formation of the sparingly soluble *sym.*-di-α-naphthyl urea. It has been found possible to prepare very quickly in this way benz-a-naphthalide from one cc. of a 0.05 *N* solution of phenylmagnesium bromide.

The a-naphthalides were identified in each case by a mixed melting point determination with the amide prepared from a-naphthylamine and the appropriate acid chloride.

TABLE I

DATA ON NAPHTHALIDES

RX used in preparation of RMgX	α-Naphthalide	M. p.,[a] °C.
Methyl iodide	Acet-	160
Ethyl bromide	Propion-	126
n-Propyl bromide	n-Butyro-	121
n-Butyl bromide	n-Valero-	112
Cyclohexyl bromide	Hexahydrobenz-[b]	188
Benzyl chloride	Phenylacet-[b]	166
β-Bromostyrene	Cinnamyl-[b]	217
Bromobenzene	Benz-	161
p-Bromotoluene	*p*-Tolu-[b]	173
α-Bromonaphthalene	α-Naphtho-[b]	236

[a] The melting points recorded here are uncorrected.

[b] No reference to this a-naphthalide was found in the literature.

Summary

Reactive organometallic compounds may be conveniently identified by the formation of a-naphthalides from a-naphthyl isocyanate.

AMES, IOWA

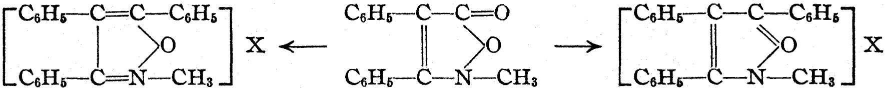
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PSEUDO BASES AND THEIR SALTS IN THE ISOXAZOLE SERIES

BY E. P. KOHLER AND A. H. BLATT

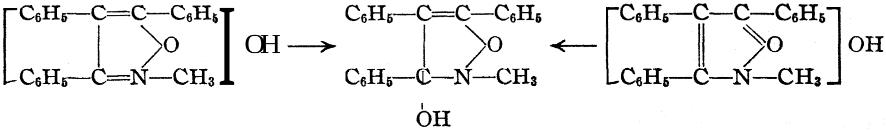
RECEIVED JANUARY 31, 1928 PUBLISHED APRIL 5, 1928

In a preceding paper[1] it was shown that when diphenyl isoxazolone is methylated by any method that is applicable it always yields an N-methyl derivative. Since this methyl isoxazolone does not have the hydrogen necessary for enolization, it would be expected to react with organic magnesium compounds to form salts of the corresponding hydroxy isoxazoline. These should be interesting because hydroxy isoxazolines are so constituted as to be capable of forming isomeric ammonium and oxonium salts.



II I III

Opinions might differ with regard to the possibility of this kind of isomerism, but all would agree, doubtless, that in the absence of color it would be difficult to identify isomers that bear this relation to each other, and also that the corresponding ammonium and oxonium hydroxides would readily undergo rearrangement to the same pseudo base.



IV

We have studied these relations with the salts of methyl triphenyl hydroxy isoxazoline (IV). Since these salts can be obtained by the action of methylating agents on triphenyl isoxazole as well as by the reaction between phenyl magnesium bromide and N-methyl diphenyl isoxazolone, there is no question about the position of the methyl and phenyl groups. Of the various salts of the isoxazoline, the sparingly soluble ferric chloride "double salt" proved to be the most satisfactory for the purpose of isolation. This salt was obtained in almost the calculated quantity by treating triphenyl isoxazole with dimethyl sulfate, hydrolyzing the resulting methyl sulfate with strong hydrochloric acid and adding ferric chloride to the solution. It was also obtained by digesting N-methyl diphenyl isoxazolone with phenyl magnesium bromide, acidifying the product with hydrochloric acid and adding ferric chloride to the aqueous layer.

From the ferric chloride double compound other salts can be made at will by liberating the corresponding base and treating it with acids. The

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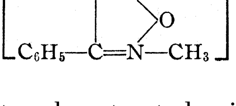
[1] Kohler and Blatt, THIS JOURNAL, 50, 504 (1928).

most interesting of these salts is the bromide. This separates in a crystalline form when the Grignard product is acidified with hydrobromic acid and, when it is obtained in this manner, is lemon yellow in color. It retains this color when recrystallized from acetone and ether or from methyl alcohol and ether, and when the base formed by treating it with sodium hydroxide is dissolved in hydrobromic acid, the product again is yellow.

A colorless bromide can be made by an indirect method. Like many other bromides of pseudo bases, the yellow salt readily combines with bromine to form an orange-colored perbromide which is sparingly soluble and easily purified. This perbromide is capable of brominating acetone and its solution in acetone on addition of anhydrous ether deposits a colorless bromide which can be recrystallized without acquiring color.

Unfortunately both the yellow and the white bromides are difficult to handle, and neither could be obtained in a form in which it gave consistent analytical results; mean values for bromine agreed closely with the calculated, but individual values obtained with different preparations ranged nearly 2%. These bromides constitute the only indication that isomerism of the type represented by formulas II and III is possible and here the evidence is manifestly quite inadequate. A somewhat similar observation was made by Mumm and Münchmeyer[2] while studying the methylation product of phenyl isoxazole, but in that case also the evidence is inadequate.

When the isomeric bromides are treated with concentrated hydrochloric acid and ferric chloride, they give the same double chloride, and both lose methyl bromide readily when heated; the melting points obtained, therefore, by heating the individual bromides, mixtures of the two and mixtures with triphenyl isoxazole are the same as those obtained for the pure isoxazole. In the absence of any conclusive evidence as to their structure, we shall, for the present, represent all of the salts as cyclic ammonium compounds



· FeCl$_4$, Br, Br$_3$, OC$_6$H$_2$(NO$_2$)$_3$

V VI VII VIII

These salts when treated with alkali yield an exceedingly unstable, colorless oil. Inasmuch as this oil is insoluble in water and readily soluble in ether, it cannot be the true base, and since it regenerates the salts when it is dissolved in acids it must be the pseudo base corresponding to these salts. Moreover, when the salts are treated with alkali in the presence of methyl alcohol, the product is a stable solid methyl ether which, like ethers of other pseudo bases, likewise regenerates the salts when

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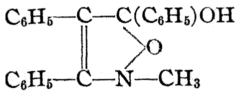
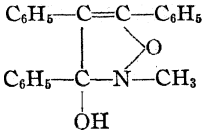
[2] Mumm and Münchmeyer, Ber., 43,3340 (1910).

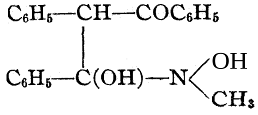
treated with acids. For the pseudo base three formulas are, *a priori*, equally probable:



IX

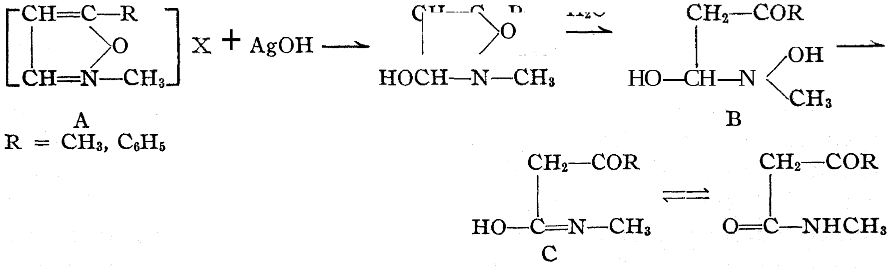


IV



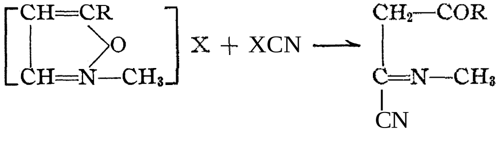
IVa

Formula IX represents the type of pseudo base that most frequently occurs in condensed ring systems[3] but which is found also in some mononuclear compounds, particularly in the bases formed from the simpler oxonium salts of dimethyl pyrone.[4] While the properties of our base could be reconciled with it, this formula is inconsistent with the behavior of the salts of less highly substituted isoxazolines. Thus, Claisen[5] found that silver hydroxide converts the methyl iodide addition product of 5-methyl isoxazole into aceto-acet methylamide, and Mumm and Münchmeyer[6] obtained the corresponding benzoyl-acet methylamide by the action of sodium hydroxide on the methyl sulfate addition product of 5-phenyl isoxazole. These results can be accounted for only if the intermediate pseudo base has an hydroxyl group in the 3-position, in which case the mechanism of these transformations is the following.



R = CH_3, C_6H_5

In accordance with this mechanism Mumm and Bergell[7] found that potassium cyanide converts these same salts into the nitriles corresponding to the enolic modification of the acid amide.



When this mechanism, which accounts for the observed behavior of all known isoxazoles and alkali, is applied to our substances it becomes

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[3] Decker, *J. prakt. Chem.*, [2] *45*, 195 (1892).

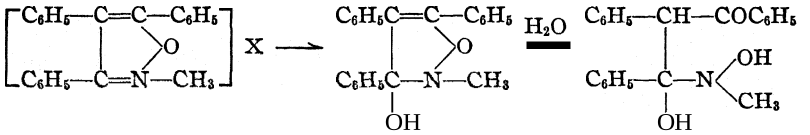
[4] Baeyer and Piccard, Ann., 384, 208 (1911); 407, 332 (1915).

[5] Claisen, *Ber.*, 42, 67 (1909).

[6] Ref. 2, p. 3344.

[7] Mumm and Bergell, *Ber.*, 45,3049 (1912).

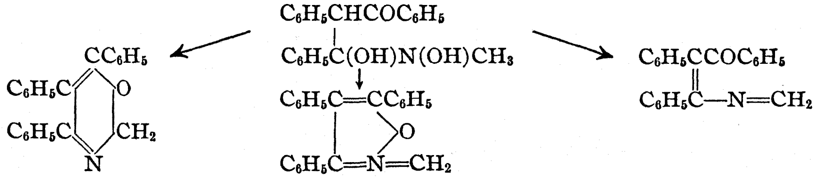
evident why here, for the first time in the isoxazole series, it has been possible to obtain a pseudo base and its ethers. For, in our substances, the presence of a phenyl group instead of a hydrogen atom in the 3-position makes impossible the loss of water corresponding to the passage of the open chained hydroxylamine derivative B into the enolic form of the acid amide C.



IV IVa

Whether our liquid pseudo base corresponds to IV or to the open-chain hydrolysis product IVa could not be established but since the composition of our ethers corresponds to derivatives of the cyclic form IV this doubtless represents a step in the process.

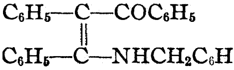
The presence of the phenyl group in position 3 in our pseudo base prevents the loss of water in the fashion observed in the unsubstituted isoxazolines, so with this pseudo base water is lost in a different manner and an entirely different set of consequences ensues. Thus, ethereal solutions of the pseudo base gradually deposit a colorless solid of which the composition and molecular weight correspond to those of a substance formed from IVa by the loss of two molecules of water. This anhydro compound combines with picric acid and with methyl alcohol to form substances which are isomeric with the picrate and methyl ether of the pseudo base. The process by which the anhydro compound is formed is not reversible, and neither the anhydro compound itself nor any of its derivatives can be transformed into salts of the pseudo base. Instead, the anhydro compound and all of its derivatives when treated with acids lose their nitrogen and yield phenyl dibenzoyl methane. These substances, therefore, belong to an entirely different class of compounds. Since a part of the hydrogen lost as water is necessarily contributed by the methyl group the number of possible formulas is limited.



X XI XII

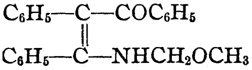
Few metoxazines (X) have been made and little is known about them except that they are easily hydrolyzed to open chained compounds. By assuming that the ring is opened in the proper manner by alcohol, alcoholates, halogen acids, picric acid and organic magnesium compounds, it would be possible to interpret most of the reactions of the anhydro compound with formula X. This formula, however, does not account for the most characteristic property of the substance—its autoxidation in moist air with liberation of formaldehyde.

Formulas XI and XII represent new types of compounds. All the facts at present available can be explained equally well with either of these formulas. Thus, ozonization results in equivalent quantities of benzil and benzoic acid; hydrolysis gives phenyl dibenzoyl methane; and phenyl magnesium bromide leads to an addition product which gives benzil when ozonized and phenyl dibenzoyl methane and benzyl amine when hydrolyzed. It is evident from these results that in order to distinguish between formulas XI and XII it will be necessary to prepare an anhydro compound in which the hydrocarbon residue in the 3-position is not a phenyl group. For the present we shall tentatively adopt formula XII and therefore represent the addition products as follows.



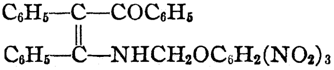
$$\begin{array}{l} C_6H_5{-}C{-}COC_6H_5 \\ \qquad\ \ \| \\ C_6H_5{-}C{-}NHCH_2C_6H_5 \end{array}$$

XIII



$$\begin{array}{l} C_6H_5{-}C{-}COC_6H_5 \\ \qquad\ \ \| \\ C_6H_5{-}C{-}NHCH_2OCH_3 \end{array}$$

XIV



$$\begin{array}{l} C_6H_5{-}C{-}COC_6H_5 \\ \qquad\ \ \| \\ C_6H_5{-}C{-}NHCH_2OC_6H_2(NO_2)_3 \end{array}$$

XV

In solutions these addition products may be in equilibrium with the anhydro compound or with their tautomeric modifications, but owing to the mode of addition they cannot regenerate an hydroxylamine derivative and therefore cannot revert to the pseudo base and the salts.

The formation of the anhydro compound and of addition products isomeric with derivatives of the pseudo base is a novelty in the chemistry of ammonium and oxonium compounds. Other pseudo bases are unstable: some are so easily oxidized that only the corresponding ketones can be isolated;[8] others lose water and form ethylenic derivatives;[9] many pass into open chained compounds.[10] All known pseudo bases of the isoxazole series are unstable; they combine with water to form open chained disubstituted hydroxylamines, and when these are so constituted that they cannot lose water in any other way they pass into a highly unsaturated, completely conjugated anhydro compound.

Experimental Part

I. *Salts*

The ferric chloride double salt is most conveniently obtained from the addition of triphenyl isoxazole and dimethyl sulfate, the yellow bromide from the reaction between methyl-diphenyl isoxazolone and phenyl magnesium bromide, and the picrate from the methyl ether of the pseudo base. Methylation of the isoxazole presents no complications, but the Grignard reaction yields two products, of which one remains in the

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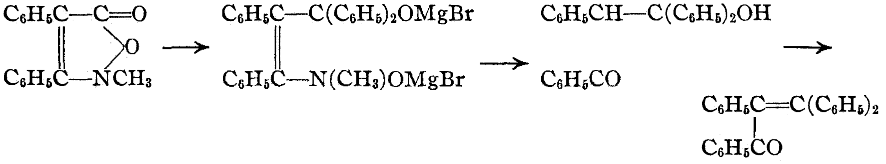
[8] Ref. **3,** p. **161.**

[9] Decker and Hock, *Ber.,* **37, 1564 (1904);** Decker and Pschorr, *ibid.,* p. **3396.**

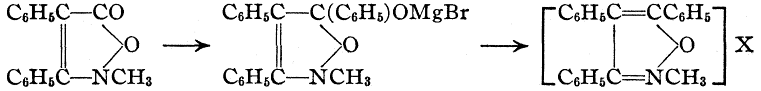
[10] Zincke, *Ann.,* **330,361 (1903); 333,296 (1904).**

ethereal layer after the magnesium derivatives have been decomposed with acids while the other enters the aqueous solution as a salt.

Two products are formed in this case because the Grignard reaction may start either by opening the ring or by adding to the carbonyl group. When it starts by opening the ring the primary product is a ketone which immediately combines with a second molecule of the reagent, and when the resulting magnesium derivative is acidified it yields diphenyl benzalacetophenone.



When the Grignard reagent combines with the carbonyl group of the isoxazolone it forms a magnesium derivative that yields a salt when acidified.



In accordance with this interpretation we found that the yield of diphenyl benzalacetophenone (10–15%) is not increased either by the use of a large excess of reagent or prolonged heating.

The Ferric Chloride Double Salt, V.—Ten g. of pure triphenyl isoxazole was added, in portions, to 30 g. of pure dimethyl sulfate. The mixture was heated on a steam-bath until the isoxazole had dissolved completely and did not reprecipitate on cooling, then cooled and treated with half-concentrated hydrochloric acid in order to decompose the excess of reagent and convert the addition product into a water-soluble salt. Next ferric chloride solution (two parts of chloride to one of water) was added until the double salt was precipitated. The crude product was washed with a little water and then recrystallized from glacial acetic acid.

Anal. Calcd. for $C_{22}H_{18}ONFeCl_4$: C, 51.8; H, 3.6; Cl, 27.8. Found: C, 51.4; H, 3.6; Cl, 27.8.

The salt crystallizes well from all common solvents except ether and petroleum ether in which it is very sparingly soluble. In glacial acetic acid it is very soluble at the boiling point and very slightly soluble at the ordinary temperature. It separates in sulfur-yellow needles and melts at 162°.

The Grignard Reaction.—When an ethereal solution of 2-methyl-3,4-diphenyl isoxazolone is added to phenyl magnesium bromide it forms a white, curdy precipitate which on stirring turns into a heavy, dark green oil. If the mixture is decomposed at this point it regenerates the methyl isoxazolone, and if it is heated immediately the yield of Grignard products is poor. Our procedure, therefore, was as follows. A solution of 5 g. of the isoxazolone in 100 cc. of ether was added in the course of several minutes, at room temperature and with stirring, to a solution of phenyl magnesium bromide containing 2.4 g. of magnesium. The mixture was stirred for an hour at the ordinary temperature, then boiled until the dark green oil had changed into a yellow powder. Solution and powder were then poured into a mixture of 50 cc. of hydrobromic acid (40%) and 100 g. of ice and the ether and water layers separated.

The ether layer was distilled with steam to remove ether, bromobenzene and diphenyl. The residue was an oil, and a dried ethereal solution on evaporation also left an oil, but when this was dissolved in methyl alcohol, the solution gradually deposited a solid. This was recrystallized from methyl alcohol, from which it separated in small, colorless prisms melting at 149–150°. An analysis led to the formula $C_{27}H_{20}O$ and the substance was identified as α,β-diphenyl benzalacetophenone by comparison with a specimen on hand;[11] yield, 0.7–1 g.

The Yellow Bromide, **VI.**—The water layer from the Grignard reaction gradually deposited a yellow salt which was collected and air dried. The substance changed in color when exposed to light and air, and it decomposed on drying under reduced pressure. Purification was attempted by solution in warm acetone and reprecipitation with ether, and also by solution in methyl alcohol and precipitation with ether, but it was not possible to get consistent analytical results.

Anal. Calcd. for $C_{22}H_{18}ONBr$: Br, 20.4. Found. Br, 20 7, 19.1.

When heated the substance loses methyl bromide at comparatively low temperatures, then melts at 209–210°—the melting point of triphenyl isoxazole. **A** specimen heated to constant weight at 135" until it was colorless and free from bromine lost 27.5% instead of 24.27, calculated.

The Perbromide, **VII.**—When the aqueous layer obtained by decomposing the Grignard product with ice and hydrobromic acid was treated with excess of bromine it deposited the perbromide in minute, orange-colored crystals. The salt was readily recrystallized from hot methyl alcohol; m. p. 152°; yield from 5 g. of the isoxazolone, **8-9** *g*.

Anal. Calcd. for $C_{22}H_{18}ONBr_3$: C, 47.8; H, **3.3;** Br, 43.5. Found: C, 47.2; H, **3.3;** Br, **43.5.**

The Colorless Bromide, **VI.**—When the methyl alcoholic filtrates from the perbromide are diluted with ether they deposit a colorless salt. This is more conveniently obtained by dissolving the perbromide in acetone and gradually diluting the solution with ether. The acetone solution is yellow and has the odor of bromo acetone; on standing and on continuous dilution with ether its color fades and it precipitates a colorless salt. The colorless bromide decomposes at comparatively low temperatures and turns yellow on exposure to light. Attempts to purify it were no more successful than with the yellow bromide.

Anal. Calcd. for $C_{22}H_{18}ONBr$: Br, 20.4. Found: Br, 20.4, 21.2, 19.2. Loss in weight **at 135°:** 25.2 instead of 24.2 calcd. for CH_3Br.

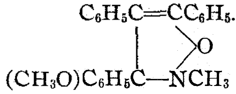
The solubilities of the yellow and white bromides appear to be the same and both form the same ferric chloride double salt and the same perbromide.

The **Picrate,** VIE.—The picrate is deposited as a yellow powder when an ethereal solution of picric acid is added to a solution of the methyl ether of the pseudo base in the same solvent. By recrystallization from methyl alcohol or ethyl acetate containing picric acid, it is obtained in yellow needles melting at 174°.

Anal. Calcd. for $C_{28}H_{20}O_8N_4$: C, 62.2; H, 3.7. Found: C, 62.3; H, 3.8.

II. The Pseudo Base and its Ethers

The pseudo base was obtained only as an oil that rapidly changed to other substances. Its composition and character are inferred from those of its ethers, which may be obtained either by dissolving the oil in alcohols or, better, by treating the salts with alcoholates or alcoholic solutions of sodium hydroxide.

The Methyl Ether, 

$$\begin{array}{l} C_6H_5C{=}CC_6H_5 \\ \quad | \qquad \quad \rangle O \\ (CH_3O)C_6H_5C{-}NCH_3 \end{array}$$

.—When a 5% solution of sodium in methyl alcohol was added to the yellow bromide considerable heat was evolved and the

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[11] Kohler, ***Am.*** *Chem. J.*, **38,** 559 (1907).

mixture soon became a stiff paste. This was diluted with water and then extracted with ether. The ethereal solution was freed from methyl alcohol with a saturated solution of calcium chloride, then dried and concentrated. It deposited a solid in stout prisms. After recrystallization from methyl alcohol the solid melted, with decomposition, at 135°.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.4; H, 6.2; OCH_3, 9.0. Found: C, 80.1; H, 6.4; OCH_3, 9.3.

The methyl ether dissolves in strong hydrochloric acid and gives a clear solution which on addition of ferric chloride precipitates the double chloride melting at 162°. It dissolves also in 15% hydrobromic acid and this solution deposits the yellow bromide.

The ethyl ether was obtained as a micro-crystalline powder melting at 118°.

Anal. Calcd. for $C_{24}H_{23}O_2N$: C, 80.7; H, 6.4. Found: C, 80.4; H, 6.6.

The ethyl ether reacts with acids like the methyl ether and forms the same salts. When its solution in boiling methyl alcohol is cooled it deposits the methyl in place of the ethyl ether.

The Pseudo Base, IV or ma.—The reaction between the salts and aqueous alkali is illustrated by the following experiment. Four g. of the yellow bromide was shaken in a separatory funnel with an excess of 5% sodium hydroxide in the presence of 75 cc. of alcohol-free ether. A part of the ether was removed after shaking for only a few minutes and while most of the salt still remained unattacked. This ethereal solution was washed with water, rapidly dried with sodium sulfate and concentrated in a current of air. The concentrated solution gave the methyl ether of the pseudo base when mixed with methyl alcohol, the picrate melting at 174°, and on complete evaporation left an oil which likewise gave the methyl ether melting at 135°.

The rest of the material in the separatory funnel was shaken until all of the salt had disappeared. The ethereal layer was washed with water, thoroughly dried with sodium sulfate, then concentrated in a current of air. A sample removed at this stage still gave the picrate melting at 174°, but when another sample was mixed with methyl alcohol anti boiled until the ether had been expelled, it gave in place of the methyl ether melting at 135° an isomeric methoxyl compound melting at 104–105°. On further evaporation the ethereal solution deposited colorless needles of the anhydro compound.

The Anhydro Compound, XII.—The anhydro compound is formed whenever ethereal solutions of the pseudo base are prepared essentially as described in the preceding experiment. The yield appears to be independent of the concentration of the alkali and the time during which it is allowed to act. Thus the concentration of the base was varied between 5 and 40%, and the time between thirty minutes and twelve hours without appreciably affecting the yield, which in all cases was about 50%. The substance separates in colorless needles which rapidly turn yellow, superficially, when exposed to the air. It was purified by recrystallization from absolute ether and from acetone that had been distilled from permanganate. It then melted at 140–141°. A qualitative test proved the presence of nitrogen and a negative Zeisel determination showed the absence of alkoxyl groups.

Anal. Calcd. for $C_{22}H_{17}ON$: C, 84.9; H, 5.5. Found: C, 84.7; H, 5.8.

In freezing benzene the molecular weight was found to be 306 instead of the calcd. 311.

The anhydro compound is colorless but even the purest samples turn yellow in the air. The nature of the change has not been established; it is accompanied by the liberation of formaldehyde, the odor of which is always perceptible in the containers in which the substance is kept.

Hydrolysis by Acids.—Acids are incapable of regenerating the salts from the anhydro compound. Thus 15% hydrobromic acid turned the substance into a yellow oil which gradually solidified and finally when heated with the acid gave phenyl dibenzoyl methane melting at 146–147°. Similarly, when aqueous hydrochloric acid was added to a solution of 0.7 g. of the anhydro compound in methyl alcohol, the solution turned yellow, but the color faded on heating and the colorless solution, when cooled, deposited the calculated amount of phenyl dibenzoyl methane. This was identified by comparison with an authentic sample.

Reaction with Phenyl Magnesium Bromide, **XIII.**—A solution of 2 g. of the anhydro compound in anhydrous ether was added to phenyl magnesium bromide made from 1 g. of magnesium. The resulting clear green solution was boiled for half an hour, then cooled and poured into ice and ammonium chloride. The ethereal layer when dried and evaporated left a colorless solid which after recrystallization from methyl alcohol melted at 134°. The yield was quantitative.

Anal. Calcd. for $C_{28}H_{23}ON$: C, 86.4; H, 5.9. Found: C, 86.0; H, 6.1.

Hydrolysis of the Addition Product.—Ten cc. of pure, concentrated hydrochloric acid was added to a solution of 3.9 g. of the addition product in 30 cc. of methyl alcohol. The intensely yellow solution was heated on a steam-bath for five minutes during which it became colorless and deposited a heavy precipitate of phenyl dibenzoyl methane. After an hour's heating the mixture was cooled and filtered and the solid washed with methyl alcoholic hydrochloric acid. The filtrate was extracted with ether. The ethereal layer on evaporation gave a second crop of the diketone, making the total yield 2.85 g., equal to 95%.

The aqueous layer was evaporated to dryness; it left a discolored hydrochloride (1.49 g. instead of 1.43 g. calcd.). A solution of 1.6 g. of sodium hydroxide in 15 cc. of water was added to the dry hydrochloride; it liberated an oil which had the odor of benzyl amine and which rapidly changed to a granular solid when 2.1 g. of benzoyl chloride was added to the alkaline suspension. After washing and drying, the crude solid melted at 104–105°, and it caused no depression of the melting point of an authentic sample of benzoyl benzylamine. The yield was 2.05 g., equal to 97%.

Action of **Ozone.**—Ozonized oxygen containing approximately 6% of ozone was passed for two hours through a solution of 2 g. of the Grignard product in carbon tetrachloride. Both the solid ozonide that separated and the oil left after the removal of the solvent were decomposed with water in the usual manner. The ethereal solution of the product deposited a solid which after recrystallization from methyl alcohol, melted at 92–94° and caused no depression in the melting point of pure benzil.

The Methyl Alcohol Addition Product, **XIV.**—A solution of 1 g. of the anhydro compound in 30 cc. of methyl alcohol was boiled for an hour, then concentrated and cooled. It deposited 0.85 g. of a compound melting at 104°. The same substance was obtained as one of the products formed by the prolonged action of sodium methylate on its isomer, the methyl ether of the pseudo base. In this case 2.9 g. of the methyl ether, when boiled for five hours with 10 cc. of a 4% solution of sodium methylate, gave 1.1 g. of the new methoxyl compound.

Anal. Calcd. for $C_{23}H_{21}O_2N$: C, 80.4; H, 6.2; OCH_3, 9.0. Found: C, 80.2; H, 6.1; OCH_3, 9.2.

The Picric Acid Addition Product, **XV.**—Toward mineral acids the methyl alcohol addition product behaves precisely like the Grignard product, forming a yellow solution which fades on warming and ultimately yields phenyl dibenzoyl methane. Toward picric acid, on the other hand, the addition product behaves like the anhydro compound itself. Thus when an ethereal solution of picric acid is added to a solution of the addition product in the same solvent a yellow solid separates, which contains no methoxyl, is identical with the product obtained from the anhydro compound, and is isomeric with the picrate of the pseudo base. After recrystallization from glacial acetic acid this yellow product melts at 184°. Like all the other addition products of the anhydro compound it is readily hydrolyzed to phenyl dibenzoyl methane.

Anal. Calcd. for $C_{28}H_{20}O_8N_4$: C, 62.2; H, 3.7. Found: C, 61.9; H, 3.8.

Summary

This paper contains the results of the study of the pseudo base 2-methyl-3,4,5-triphenyl-3-hydroxy isoxazoline and its salts. It is shown that this substance, in addition to the usual reactions of pseudo bases, undergoes a novel irreversible transformation into an open chained anhydro compound, the behavior of which has been explored. The results obtained in this work provide a basis for the formulation of a mechanism which correlates the behavior of all pseudo bases of the isoxazole series.

CAMBRIDGE 38, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MISSISSIPPI COLLEGE]

PREPARATION OF ALIPHATIC AND AROMATIC SULFONES WITH SODIUM HYPOCHLORITE[1]

BY A. E. WOOD AND ELLIS G. TRAVIS

RECEIVED FEBRUARY 21, 1928 PUBLISHED APRIL 5, 1928

This paper represents a study of the conditions best suited for the oxidation of pure alkyl and aromatic sulfides. Birch and Norris[2] have made some observations relevant to the oxidation of organic sulfides previously dissolved in a light petroleum distillate. Birch and Norris reported the complete oxidation of ethyl, n-propyl, *iso*butyl and *iso*-amyl sulfides to the corresponding sulfones. Under similar conditions, Wood, Greene and Provine[3] reported the oxidation of ethyl, n-propyl and phenyl sulfides to the corresponding sulfones.

Experimental

Eastman's ethyl, n-propyl, n-butyl, n-heptyl, phenyl and benzyl sulfides were used without further purification.

Hypochlorite solutions 1, 2 and 3 were prepared by passing chlorine into solutions of pure sodium hydroxide. Hypochlorite solutions 4, 5 and 6 were prepared by passing chlorine into solutions containing both pure sodium hydroxide and pure sodium carbonate. The chlorinating solutions were kept below 27°. The alkalinity was determined by decomposing the sodium hypochlorite with hydrogen peroxide and titrating against standard hydrochloric acid with phenolphthalein and methyl orange as indicators. The available chlorine was determined by titrating the iodine liberated from potassium iodide against 0.1 N sodium thio-

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[1] A preliminary version of this paper was received on May 3, 1927.

[2] Birch and Norris, J. *Chem. Soc.*, *127,* 1934 (1925).

[3] Wood, Greene and Provine, *Ind.* Eng. *Chem.*, 18,823 (1926).

sulfate solution. The compositions of the hypochlorite solutions are indicated in Table I.

Table I

Compositions of Sodium Hypochlorite Solutions

NaOCl soln.	NaOH, %	Na_2CO_3, %	Avail. Cl per liter, g.
1	2.00	0.00	93
2	0.20	.00	23
3	.11	.00	91
4	.00	.12	23
5	.00	.23	23
6	.00	.61	23

In carrying out the experiments, from 0.2 to 0.3 g. of the organic sulfide was added to 50 cc. of the sodium hypochlorite solution previously placed in a small, glass-stoppered bottle and shaken for predetermined periods of time. The sulfones were recovered, recrystallized and identified by melting point determinations.

Results

The results with the different hypochlorite solutions are indicated in Table II.

Table II

Results with Different Solutions

NaOCl soln.	Ethyl sulfide	n-Propyl sulfide	n-Butyl sulfide	n-Heptyl sulfide	Phenyl sulfide	Benzyl sulfide
1	Completely oxidized in two hours	Partially oxidized in two hours	No appreciable effect at the end of a two-hour treatment			
2 3	Oxidized instantly	Oxidized within thirty minutes	Oxidized within three hours	Slight effect	Oxidized within three hours	
4 5 6	All organic sulfides investigated except n-heptyl were almost instantly converted to the corresponding sulfones. With the n-heptyl sulfide small amounts of the sulfone were formed but the oxidation was principally to the sulfoxide.					

An examination of Table II indicates that ethyl, n-propyl, n-butyl and n-heptyl sulfides are reactive in the order named and that phenyl and benzyl sulfides have about the same order of reactivity as the n-butyl sulfide. Table II also indicates the effects of hydroxyl concentrations on the reactivity of sodium hypochlorite solutions. Sodium hypochlorite solution 1 was apparently reactive only with ethyl and n-propyl sulfides. Solutions 2 and 3 were apparently only slightly reactive with n-heptyl sulfide but were reactive with the other alkyl sulfides investigated in an inverse ratio to the molecular weights. The aromatic sulfides investigated were reactive with solutions 2 and 3. Solutions 4, 5 and 6 were most reactive, readily converting all the sulfides investigated except n-heptyl to the corresponding sulfones. These last sodium hypochlorite solutions converted n-heptyl sulfide principally to the sulfoxide, forming at the same time small amounts of the n-heptyl sulfone.

It is also interesting to note that the alkalinity of sodium hypochlorite solutions 4, 5 and 6 is due to sodium carbonate, thereby stabilizing the solution for use and at the same time reducing the hydroxyl concentration to a minimum and promoting the formation of free hypochlorous acid in accord with the theory of Kauffmann.[4] These facts are also in agreement with the results obtained by Cullen and Hubbard,[5] who state that hypochlorite solutions may be stabilized for use by the addition of 0.5% of borax, by the addition of 1% of sodium carbonate, or by the addition of 0.2% of sodium hydroxide.

Conclusions

These results indicate that sodium hypochlorite solutions of low alkalinity may be effectively used in the preparation of aromatic sulfones and low molecular weight alkyl sulfones from the corresponding sulfides.

Summary

This work represents a study of the action of solutions of sodium hypochlorite on a number of selected organic sulfides. Ethyl, n-propyl, n-butyl, n-heptyl, phenyl and benzyl sulfides were used. Sodium hypochlorite solutions of varying degrees of alkalinity and available chlorine were employed. These results indicate that the oxidizing effects of solutions of sodium hypochlorite are dependent on the alkalinity of the hypochlorite solution and on the type and molecular weight of the organic sulfide employed. With hypochlorite solutions of low alkalinity (about 0.2% of free sodium hydroxide) ethyl and n-propyl sulfide were readily and completely converted to the corresponding sulfones; butyl, phenyl and benzyl sulfides were less readily converted to the corresponding sulfones; and heptyl sulfide was the least reactive, being converted principally to the sulfoxide.

CLINTON, MISSISSIPPI

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[4] Kauffmann, *Z. angew. Chem.*, **37**, 364 (1924).

[5] Cullen and Hubbard, *J. Biol. Chem.*, **37**, 611 (1919).

NOTES

The Preparation of *p*-Iodo-anisole.—A convenient method for the preparation of *p*-iodo-anisole has been described by Brenans,[1] through the interaction of an alcoholic solution of anisole with mercuric oxide and iodine. We prepared a considerable quantity of iodo-anisole from the above-mentioned compounds but found it advisable to modify the method in several essential respects. Only one-half of the amount of iodine used by Brenans is necessary; furthermore, carbon tetrachloride is a more suitable solvent than alcohol and an elevated temperature seems to exert a favorable influence on the course of the reaction. A three-necked, round-bottomed, liter flask was fitted with a mechanical stirrer in the following manner. A short piece of rubber tubing was attached to one end of a short glass tube and the other end of the latter was passed through a cork which fitted the large neck of the flask. The stirrer was then inserted into the glass tube, which served as a guide for the shaft of the stirrer, and the rubber tube which fitted the stirrer shaft tightly prevented the escape of liquid around the latter. The two smaller necks of the flask were fitted with an inlet and an outlet tube, respectively. The inlet tube was closed with a calcium chloride bulb and ended about two inches above the surface of the reaction mixture. The outlet tube was attached to a small Drechsel wash bottle, which served as a trap and was cooled with ice. The Drechsel bottle was connected to a suction pump. Forty-three and two-tenths g. of anisole (0.4 mol. equivalent), 200 cc. of *dry* carbon tetrachloride and 23.2 g. of yellow mercuric oxide (the total amount of mercuric oxide added was 53.2 g. or 0.5 mol. equivalent) were put into the flask and stirred rapidly. Iodine was then added in approximately. 10g. portions until 100.8 g. (0.4 mol. equivalent) had been added. The remainder of the mercuric oxide was added in two parts, a 20g. and a 10g. portion during the course of the reaction. During the addition of the iodine the reaction mixture was heated to 50–60° and a fairly rapid stream of air was sucked through the flask. Carbon tetrachloride, iodine and water collected in the trap and at intervals this mixture was removed, dried with calcium chloride and then returned to the reaction flask.

After four hours the reaction mixture was filtered, the inorganic residue thoroughly washed with hot carbon tetrachloride and the carbon tetrachloride filtrate was shaken with sodium bisulfite solution and finally with a small amount of potassium iodide solution in order to remove any unchanged iodine and dissolved mercuric iodide. The carbon tetrachloride layer was dried with fused sodium sulfate and distilled. The portion which boiled below 200° was discarded and the residue in the distilling flask was poured into an evaporating dish and allowed to crys-

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[1] Brenans, *Bull. soc. chim.*, [3] 25,819 (1901).

tallize. Any oil present was drained off and the product was then recrystallized from 25 cc. of alcohol, filtered and washed with a small amount of the same solvent. The average yield of pure material was 69 g. or 73% of the calculated amount; m. p. 49–52". In order to determine whether or not the product was contaminated with the higher boiling di-iodo-anisole, 110 g. of the purified iodo-anisole was distilled. The product boiled at 139–139.5' and not more than a gram of residue remained in the distillation flask.

When the reaction was carried out at ordinary temperature the average yield of *p*-iodo-anisole from two experiments was 57%.

Iodine is rapidly decolorized by mercuric oxide in the presence of water. In one instance a mixture of iodine, mercuric oxide and water was stirred until the iodine was completely decolorized. Anisole was then added and the mixture was stirred again for eight hours. No iodo-anisole was produced. It is obvious that the removal of water formed during the preparation of iodo-anisole is desirable. When the water given in the reaction was not removed by a stream of air we found that in addition to mercuric iodide a colorless, inorganic compound was formed. This substance liberated iodine from acidified potassium iodide solution and was, no doubt, mercuric iodate resulting from decomposition of the unstable mercuric hypo-iodite, one of the initial products of the interaction of iodine, mercuric oxide and water.

We found that iodine did not react with anisole if mercuric oxide was replaced by lead oxide or calcium oxide. If the mercuric oxide merely serves to destroy the equilibrium

$$CH_3OC_6H_5 + I_2 \rightleftharpoons CH_3OC_6H_4I + HI$$

as is ordinarily supposed, it seems strange that lead oxide and calcium oxide should be inactive.

Although anisole can be mercurated quite readily[2] and the following series of reactions can be carried out during the course of four to five hours, this method for the preparation of *p*-iodo-anisole is impractical since the final reaction product consists of a mixture of anisole, *o*- and *p*-iodo-anisole and di-iodo-anisole.

$$CH_3OC_6H_5 + Hg(OCOCH_3)_2 = CH_3OC_6H_4{-}HgOCOCH_3 + CH_3COOH$$
$$CH_3OC_6H_4{-}HgOCOCH_3 + NaCl = CH_3OC_6H_4HgCl + CH_3COONa$$
$$CH_3OC_6H_4HgCl + I_2 = CH_3OC_6H_4{-}I + HgICl$$

The above process does not gain in practicability even though it is possible to separate the *p*-anisylmercuric chloride from its ortho isomer since this operation involves considerable time and labor.

Iodine chloride reacts vigorously with anisole but there seems to be formed a complex mixture of iodo and chloro substitution products of anisole.

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[2] Dimroth, Ber., 35,2867 (1902).

By the interaction of potassium iodide with diazotized *p*-anisidine a 75–80% yield of pure *p*-iodo-anisole can be obtained.

CONTRIBUTION FROM THE
COLLEGE OF PHARMACY OF THE
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F. F. BLICKE
F. D. SMITH

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Note on the Purification of Brucine.[1]—Brucine has come to be the alkaloid most commonly used in resolving optically active acids. The free base can be recovered after the resolution and used over and over. If one tries to obtain the alkaloid by precipitating it with ammonium hydroxide from a solution of the hydrochloride, the result is a paste which is difficult to filter and impossible to wash adequately.

The following procedure gives a crystalline product of a high degree of purity. To the solution of brucine hydrochloride is added about one-fifth its volume of ethyl alcohol. The solution is then made definitely alkaline with ammonium hydroxide. After standing for several hours crystals begin to appear. Sometimes twenty-four to forty-eight hours or even longer must elapse before crystallization starts. In about a week the precipitation is complete. The crystals are filtered, washed and air-dried. They are then ready for use again in resolution.

CONTRIBUTION FROM THE
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A Variation of the Carius Method for the Determination of Sulfur.—Among the various modifications of the Carius method for the determination of sulfur, it is frequently suggested that bromine[1] or a few crystals of potassium bromide[2] be added to the fuming nitric acid. This modification probably arose through the observation that halogenated compounds are more readily oxidized.[3] Rupp[4] introduced the variation of placing a barium salt in the tube with a marked shortening of the time required to gather the resulting sulfate. He was aware of Carius' observation as to the greater ease of oxidation of chlorine containing compounds but did not correlate the use of barium chloride with any observed

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[1] This work has been conducted under a grant from the Douglas Smith Foundation for Medical Research of the University of Chicago.

[1] Angeli, *Gazz. chim. ital.*, 21, [1] 163 (1891).

[2] Thorpe and Whiteley, "Students Manual of Organic Chemical Analysis," Longmans, Green and Co., London, 1926, p. 59.

[3] Carius, Ann., 116, 19 (1860).

[4] Rupp, *Chem.-Ztg.*, 32, 984 (1908).

increase in the ease or extent of oxidation. The fact that chlorine is a better halogenating agent than bromine led the authors to carry out the following series of comparative experiments on the oxidation of sulfonal by means of modifications of the Carius method.

One-tenth gram of sulfonal was oxidized by means of 3 cc. of fuming nitric acid (sp. gr. 1.60) with the addition of the substances noted below. A temperature of 200° was chosen to allow for an oxidation slow enough for comparison.

TABLE I

RESULTS OF SULFUR ANALYSES

Per cent. of Theoretical Sulfur Appearing as Sulfate

Time of heating, hrs.	I HNO_3	II HNO_3 and Br_2	III HNO_3 and $BaBr_2$	IV HNO_3 and $Ba(NO_3)_2$	V HNO_3 and $BaCl_2$	VI HNO_3 and $NaCl$
6	14.2	6.6	22.8	20.1	50.7	32.1
12	25.2	23.4	41.1	44.0	75.6	75.6
24	46.2	49.6	57.8	66.4	84.4	95.6
48	70.6	71.7	72.1	85.6	95.2	99.5

In series II four drops of bromine was used in each. In series V 0.1915 g. of barium chloride (enough to give 5% excess) was used. In III, IV and VI the salts shown were used in quantities equivalent to the barium chloride in V.

It appears from the table above that Rupp's modification is more thorough in its oxidation than either nitric acid alone or nitric acid and bromine. The use of sodium chloride also markedly increases the ease of oxidation.

Although Rupp's method has been checked[5] and extended to microanalysis,@the authors have found that too frequently the opening of the Carius tube is accompanied by chips of glass falling into the tube's contents, from which they cannot be removed. For the oxidation of those sulfur compounds which give rise to stable sulfones, the authors suggest the introduction of 0.3 to 0.4 g. of sodium or potassium chloride and 3 cc. of fuming nitric acid with the sample to be analyzed. After heating, cooling and opening, the contents of the tube, together with the washings, can be filtered and evaporated to dryness, providing sufficient sodium chloride has been used to fix the sulfate formed. The analysis can then be continued in the regular manner.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
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PRINCETON, NEW JERSEY

VICTOR C. ROGERS
GREGG DOUGHERTY

RECEIVED FEBRUARY 16, 1928
PUBLISHED APRIL 5, 1928

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[5] Schneider, *Ber.*, 42,3417 (1909).

[6] Pregl-Fyleman, "Quantitative Organic Microanalysis," Blakiston's Son and Co., Philadelphia, 1924, p. 126.

Chlorine Dioxide Explosion.—It seems proper to issue a warning as to possible danger in the oxidation of primary alcohols by means of chlorate and dilute sulfuric acid in presence of vanadium pentoxide as described by Milas.[1]

A first trial of this interesting reaction, as applied to n-butyl alcohol, was uneventful, but gave a smaller yield than was expected, and a second trial was undertaken. This had proceeded about thirty minutes beyond the addition of the specified 18 cc. of 6 N sulfuric acid (see p. 498) when a detonation of the utmost violence occurred in the reflux condenser, scattering a shower of glass with great force. The reaction flask was undisturbed by the detonation.

It must be stated that Milas' directions were in both experiments modified by use of potassium instead of sodium chlorate, and that in the second trial the quantities of 5% sulfuric acid and chlorate were increased about 10% in the hope of decreasing the amount of alcohol unattacked; after the explosion part of the chlorate was still present in solid form. At the time of the accident the liquid was boiling gently.

Communication with Dr. Milas reveals the fact that, except in the oxidation of methyl alcohol (for which a special and safer procedure is described), sixty-two trials of the method were made with no explosion. He also states the substitution of potassium for sodium chlorate to be inadmissible, the former being "much more reactive" and also more likely to cause explosion because of its lower solubility in water. Most important, there is pointed out the absolute necessity for regulating the temperature of the liquid to 75–80° during and also following any addition of fresh acid. This appears clearly stated in the general directions (p. 495), but in the specific directions the first period of heating to 75–80° is followed by a period of *boiling*, and then more acid is introduced and the "heating" is continued. Throughout the directions the word "heating" is used, in a sometimes puzzling sequence, to imply either a temperature of 75–80° or the boiling temperature of the mixture.

In the interest of safety, therefore, it seems wise to emphasize the apparently urgent need for such a control of temperature that the liquid is not above 80° when fresh acid is added, and that this temperature be not exceeded until some time after the final addition of acid has been made.

According to Dr. Milas the method is quite safe if the conditions are properly controlled. It is hoped by this emphasis upon the conditions whose control is important, the oxidation may be rendered as free from hazard as is claimed. A very vivid recollection of a storm of glass, and the fact that the ill-fated experiment, heated only about five and a

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[1] Milas, THIS JOURNAL, 50, 493 (1928).

half hours, gave a very fair yield of ester, have combined to satisfy the writer's curiosity.

HARRISON LABORATORY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA, PENNSYLVANIA

E. C. WAGNER

RECEIVED MARCH 24, 1928
PUBLISHED APRIL 5, 1928

NEW BOOKS

Oxidation-Reduction Reactions in Inorganic Chemistry. By ERIC R. JETTE, Ph.D., Assistant Professor of Chemistry, Washington Square College, New York University. The Century Company, 353 Fourth Avenue, New York, 1927. xvi + 152 pp. 10 figs. 13 × 19.5 cm. Price $1.10.

The author has discussed oxidation-reduction equations from two viewpoints: the "valence-change" and the "ion-electron" methods. The principles behind this book have been developing gradually since the publication of Ostwald's "Grundlinien der Anorganischen Chemie" about thirty years ago and have been taught from the electronic point of view in certain technical schools and colleges even before Alexander Smith in his "General Chemistry for Colleges" in 1014 brought out a scheme for balancing such equations. In recently published modern textbooks more than fifty per cent. of the equations discussed and studied are of the oxidation-reduction type. The author has attempted to explain these changes and methods of balancing equations for the student who has not had physical chemistry, the qualitative rather than the quantitative side being emphasized.

Topics discussed are: oxidation-reduction in relation to atomic structure; balancing equations of non-ionic type (valence change type) and those in aqueous solutions (ion-electron type); cell reactions and activity of metals; effect of hydrogen-ion concentration applied to manganese and nitrogen reactions; application of the ion-electron method to insoluble and weakly dissociated compounds, and the formation of complex ions in reactions in which oxidation-reduction changes take place. The book contains four appendices: the thermodynamic basis of the ion-electron method; in tabular form all common oxidizers and reducers, the main products of their oxidation-reduction action and notes on conditions of their reaction; oxidation-reduction potentials; a table of ionization constants of weak inorganic acids. References to the literature are given at the ends of chapters.

The book will appeal to students who wish to round out their cultural chemistry course, to advanced students in inorganic chemistry and to students of qualitative analysis. All teachers interested in modern ways of presenting inorganic chemical facts will be interested in reading this book.

EDWARD MUELLER

The Making of a Chemical. A Guide to Works Practice. By E. I. LEWIS, M.A., and GEORGE KING, M.Sc. John Wiley and Sons, Inc., 440 Fourth Avenue, New York. 288 pp. 27 figs. **22.5** X 14.5 cm. **Price $4.00.**

Every teacher of chemistry has been called on to give advice to the young student who is trying to decide on his career. A composite picture of such a student would show a young man of 19 or 20 who has taken one or two courses in chemistry with interest and some degree of success. But he also enjoyed his work in biology and in geology and economics. He finds it hard to decide whether he wants to become a physician, a mining engineer, a business man or a chemist, and he has rather vague notions of the probable nature of his work if he does decide to become a chemist. To such a man this book may be very helpful. It gives an insight into the problems to be met by a research chemist in a factory, the methods of attack, and the tools to be used, It makes it clear that success or failure will be judged by the results as shown in the cost records. It gives much sound advice as to the college training which will be most helpful to the young industrial chemist and as to many of the problems likely to be encountered at any early stage of his industrial career.

Although this book may serve as an interesting and useful introduction to chemical engineering, it is not suitable for use as a textbook in courses in industrial chemistry or chemical engineering. It has neither the systematic description of chemical processes or chemical commodities to be found in Thorp's "Outline of Industrial Chemistry" nor the quantitative discussion of chemical engineering principles and apparatus to be found in Walker, Lewis and McAdams.

GRINNELL JONES

Physikalisch-chemische Grundlagen der chemischen Technologie. (Physico-Chemical Principles of Chemical Technology.) By DR. GEORG-MARIA SCHWAB. Verlag von Otto Spamer, Leipzig, 1927. 130 pp. 32 figs. **25 × 18 cm. Price: unbound, RM. 10; bound, RM. 12.50.**

The author in his preface says: "What the technical chemist requires in a small book on physico-chemical technology is not the description of technical processes with the addition of the appropriate physico-chemical principles and considerations of varied character. He would certainly rather be instructed systematically in the physical chemistry which is needed by him and thereby see for himself how the technology has applied these principles or can apply them. This method of presentation is also suitable for the use of students. The splendid achievements of chemical industries and their current demands show that our colleges have done well to emphasize pure science after the manner of its old masters and thus ensure that factory practice will be learned in the factory."

The chief subjects covered are: Atomic Structure, Radioactivity and Molecular Structure (26 pages); Colloids (23 pages); States of Aggregation and the Phase Rule (25 pages); Thermodynamics and Chemical Equilibrium (27 pages); Velocity of Reactions, Catalysis and Metastable Equilibrium (13 pages); Electrochemistry (19 pages); Photochemistry (6 pages).

The varied subjects are discussed clearly but very briefly. Some industrial applications are mentioned rather than explained in detail. It seems to the reviewer improbable that an industrial chemist not already familiar with the theories discussed would be able to obtain sufficient instruction from this little book to make the applications for himself.

GRINNELL JONES

Biochemical Laboratory Methods for Students of the Biological Sciences. By CLARENCE AUSTIN MORROW, Ph.D., Late Assistant Professor of Agricultural Biochemistry, University of Minnesota. John Wiley and Sons, Inc., 440 Fourth Avenue, New York. 1927. xvii + 350 pp. 29 figs. 2 charts. 15 X 23.5 cm. Price $3.75.

The author has based this excellent manual upon a laboratory course that has been given for a number of years in the Division of Agricultural Biochemistry at the University of Minnesota. The experiments have been selected with the idea of providing the student of the biological sciences thorough laboratory training in plant chemistry as well as an introduction to biochemical research methods. From this standpoint the author has succeeded admirably. The chapter on the colloidal state (Chapter I) is comprehensive and the experiments provide an excellent opportunity for training in technique. Chapter II is concerned with the physical-chemical constants of plant saps. Chapter III is devoted to the determination of hydrogen-ion concentration and to buffer action. A method is included for determining the buffer values of wheat flour extracts. The chemistry of proteins is dealt with in Chapter IV. In addition to the usual qualitative color reactions, this chapter contains directions for the isolation of natural plant proteins, the preparation and synthesis of amino acids, and methods employed in the analysis of protein. Chapters V, VI, and VII are devoted to the carbohydrates, glucosides, and fats and fat-like substances, respectively, and include such useful methods as the quantitative estimation of lignin in wood (p. 241), the preparation of pectin from grapefruit rind (p. 236) and the extraction of sitosterol from corn oil (p. 267). Methods for studying enzymes, particularly those of plant origin, are outlined in Chapter VIII. Chapter IX deals with plant pigments, including chlorophyll and carotinoid pigments, flavone and flavonol pigments and an experiment on the anthocyanin pigments. The following topics indicate the scope of some of the experiments: Extraction of chlorophylls *a* and b (p. 307); determination of carotin in butter fat (p. 317); determination of xanthophyll in egg yolk (p. 318).

The book contains an abundant bibliography, the references pertinent to the subject of each experiment being cited at the end of that experiment.

Dr. Morrow's book should be useful both to the student and investigator, and will be welcomed as an important contribution to the teaching of biochemical laboratory methods.

MEYER BODANSKY

The Microbiology of Cellulose, **Hemicelluloses,** Pectin **and** Gums. By **A.** C. THAYSEN AND H. J. BUNKER. Humphrey Milford, Oxford University Press, London, England, **1927.** viii + **363 pp. 23 figs. 14** X **22 cm.** Price **25s.** net; $8.50.

This book of 363 pages, 23 text figures and 662 references, assembles in a convenient and logical unit much information of decided importance to agriculture and industry. While the bibliography is not complete it gives a general idea of the present state of the microbiology of cellulose and related substances.

Part I, pp. 3–23, deals with the nature of cellulose, hemicellulose, pectin and gum. Part II, pp. 27–158, is given over to a description of the organisms responsible for the destruction of cellulose and its associated substances.

On p. 37 it is stated that Bredemann's classification of *Cl. Pasteurianum,* PI. *pectinovorum* and Gr. *pectinovorum* "as one species and grouped by him under the name *Bac.* amylobacter, A. Meyer and Bredemann.. . . .is substantially correct." Because of decided differences both in morphology and physiology recent investigations have shown it unwise to group these organisms under one head. The ability of these anaerobic butyric acid forming bacteria to ferment pectin is emphasized repeatedly, for example, p. **37** and p. 162. According to Beijerinck, who worked with 15 cultures, only one fermented pectin vigorously, and in a later paper by Donker 10 anaerobic cultures were studied and only one was found to ferment pectin. Other granulose positive butyric acid forming microorganisms do not cause retting. In regard to the isolation of the so-called *Bac. amylobacter* the authors state on p. 38 that this organism is "one of the most difficult types to isolate in pure culture." Recent reports on this subject show that under anaerobic conditions and in the presence of the proper medium, isolation of these organisms is quick and comparatively easy.

The authors question the use of Lactobacillus for non-spore-forming bacteria of the lactic acid group on p. 42. However, this term as first used by Beijerinck (1901) referred to the "active lactic ferments of bacilliary form which produce levo-active acid" and at present is widely used for this great group of microorganisms.

In Chapter IV concerning the Actinomycetes no mention is made of the important papers of C. Drechsler, Bot. *Gaz.* **67,** 65–83 and 147–168, (1919), and the book of R. Lieske, 292 pp, 112 fig., Leipzig, 1921, while the classification of Orskov which deals largely with the pathogenic forms is used as a basis of grouping of these organisms.

While the systematic description of the microorganisms, pp. 27–158, will be found helpful to certain workers in this field, the reviewer believes that too much space is given to needless descriptions of the numerous fungi and actinomycetes which are found growing on cellulose. These descriptions are hardly sufficient in themselves for the identification of the organisms.

Part III, pp. 161–309, deals with the decomposition of gums, pectin, hemicelluloses, and cellulose. In the list of products of a typical fermentation of starch by the acetone butyl alcohol organisms, p. 162, no mention is made of ethyl alcohol, although it is well known that this substance makes up about 4 to 5% of the fermentation products.

In the section on ensilage and spontaneous heating of plant materials, pp. 222–238, it is stated that "it is largely on the content of these polysaccharides (cellulose and hemicelluloses) that the nutritive value of the finished silage depends." This statement is incorrect. Certainly consideration should be given to the nutritive value of starch and organic acids as well as the proteins of silage. In the description of the making of silage, no doubt the authors have tried to give representative conditions in Great Britain; quite different methods, however, are followed in America. No mention is made of a somewhat analogous fermentation, the making of sauerkraut.

The statement on p. 275 that "The sapwood, therefore, and particularly that part of it which is produced during spring, is generally more readily attacked than the thick-walled heartwood" is hardly justified by observations. The results of tests show that spring wood is more readily attacked than summer wood. Again, on p. 277, "ring scale or cubical rot" are used as synonyms although these are quite different terms. A general estimate of the loss of timber through rotting has been given by R. H. Colley, in Science 61, 107–109(1925), and is no doubt more accurate than the figures quoted from Acree, p. 280, in 1919.

The whole monograph could be condensed without loss of subject matter and with considerable gain in coordination of the material. In spite of these criticisms the book brings together in convenient form a great mass of valuable information. It is well written, fully indexed and has beautiful illustrations. For all interested in the general field of applied microbiology it will be found a useful reference book.

E. B. FRED

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[CONTRIBUTION FROM KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

CATALYTIC ACTIVITY OF HYDROCHLORIC ACID AND OF POTASSZUM AND OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION

BY ETHEL M. TERRY

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This paper reports a new formulation of the catalytic influence of hydrochloric acid in hydrolyses and related reactions. The new expression is made in terms of the so-called thermodynamic activity coefficients of the acid and the corresponding term for potassium hydroxide instead of that of potassium chloride as has been done heretofore.[1] Similar expressions are derived for the catalytic influence of potassium and sodium hydroxide. Presentation of this material seems worth while since for the first time the catalytic influence of these reagents in aqueous solution even in the presence of potassium or sodium chloride has been described in terms which are independent of measurements of the rates of the reaction. A tentative formulation of the new functions follows.

Two New Functions.—For each reaction carried out at constant temperature a so-called kinetic equation may be written which defines the rate of the reaction in terms of a characteristic coefficient and the molalities, respectively, of catalyst and reacting components. As is well known, the coefficient, $K_{\text{obs.}}$, is found not to be constant for all experiments as would be the case if all variables affecting the rate of reaction were defined in the equation. Changes in the molality of a non-electrolyte term seem to have but little to do with this effect. The principal cause of the variation of $K_{\text{obs.}}$ rests apparently in a failure to define the influence of the catalyst.

Pairs of solutions of hydrochloric acid and potassium hydroxide of like molality will now be considered since it may be assumed plausibly that the activities of the non-catalyst ions, chloride and potassium ions, are the same in the two solutions (assumption 1). Let γ be the activity coefficient[2]

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[1] See, for example, Harned and Pfanstiel, THIS JOURNAL, 44,2193 (1922).

[2] Except for the expression catalytic activity and catalytic activity coefficient which appear later, the terms activity and activity coefficient should be understood in the sense introduced by G. N. Lewis. *See* Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 255 and **328.**

of the substance indicated by the subscript; let a bracketed formula represent the molality of the substance indicated by the formula. The terms which refer to the acid solution will be marked with a prime and those without the prime should be taken as belonging to the constituents of the alkaline solution. (All γ terms in the same expression refer to solutions of like molality of hydrochloric acid and potassium hydroxide unless otherwise stated.)

Since by definition, $\gamma'_{\mathrm{Cl}^-} \times \gamma'_{\mathrm{H}^+} = \gamma'^2_{\mathrm{HCl}}$ and $\gamma_{\mathrm{K}^+} \times \gamma_{\mathrm{OH}^-} = \gamma^2_{\mathrm{KOH}}$ if, as stated above, $\gamma_{\mathrm{K}^+} = \gamma'_{\mathrm{Cl}^-}$, then for each pair of solutions

$$\gamma'_{\mathrm{H}^+}/\gamma_{\mathrm{OH}^-} = \gamma'_{\mathrm{H}^+}\gamma_{\mathrm{Cl}^-}/\gamma_{\mathrm{K}^+}\gamma_{\mathrm{OH}^-} = \gamma'^2_{\mathrm{HCl}}/\gamma^2_{\mathrm{KOH}} \tag{1}$$

In every case of hydrochloric acid catalysis for which data are available if $K_{\mathrm{obs.}}$ (defined above) is divided by the activity coefficient characteristic of the acid under the conditions of the experiment for which $K_{\mathrm{obs.}}$ was determined, the quotient is found to increase with the molality of the catalyst in the reaction mixture. Therefore on the assumption (second assumption, basically that of Arrhenius) that the active agent of the acid is the hydrogen ion and therefore that variations of $K_{\mathrm{obs.}}$ are directly proportional to the activity coefficient of the catalyst ion, the activity coefficient of the catalyst ion must be considered greater than the activity coefficient of the catalyst. The latter, of course, is the geometrical mean of the activity coefficients of the two ions of each of the catalysts under consideration.

Therefore, according to assumption 2, $\gamma_{\mathrm{H}^+} > \gamma_{\mathrm{HCl}}$ and by similar logic $\gamma_{\mathrm{OH}^-} < \gamma_{\mathrm{KOH}}$.

The terms of the right-hand side of Equation 1 are rearranged in Equation 2 in order that it may be expressed as the ratio of two terms, the one in the numerator being greater than γ_{HCl} and the one in the denominator being less than γ_{KOH} (except, of course, at infinite dilution when these terms are all equal to one).

$$\gamma'_{\mathrm{H}^+}/\gamma_{\mathrm{OH}} = (\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}})/(\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}) \tag{2}$$

Therefore,

$$\gamma'_{\mathrm{H}^+}/(\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}}) = \gamma_{\mathrm{OH}}/(\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}) = d \tag{3}$$

and d is a value defined by Equation 3.

Then for any molality of hydrochloric acid

$$\gamma'_{\mathrm{H}^+} = d\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}} \tag{4}$$

and for any molality of potassium hydroxide

$$\gamma_{\mathrm{OH}^-} = d\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}} \tag{5}$$

If K_0' is the coefficient of the reaction when the influence of the catalyst is proportional to its molality, then for reactions catalyzed by the hydrogen ion of hydrochloric acid

$$K_{\mathrm{obs.}} = K_0'\gamma_{\mathrm{H}^+} = K_0'd\gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}} \tag{6}$$

then

$$K_{\mathrm{obs}}\ (\gamma_{\mathrm{KOH}}/\gamma'_{\mathrm{HCl}}) = K_0'd \tag{7}$$

Similarly for reactions catalyzed by the hydroxide ion of potassium hydroxide

$$K_{\mathrm{obs}}\ \gamma'_{\mathrm{HCl}}/\gamma_{\mathrm{KOH}} = K\ d \tag{8}$$

and K_0 is the coefficient of the reaction when the influence of the base is proportional to its molality.

Before discussing the truth of the two tentative assumptions and the possible nature of the term d, demonstration will be made of the peculiar fact that $K_0'd$ and K_0d are constant values in the cases of ester hydrolyses and similar reactions.

Hydrolysis of Ethyl Acetate in Hydrochloric Acid Solution.—It will be remembered that if the hydrolysis of ethyl acetate is carried out in dilute aqueous solution, the reaction proceeds to an equilibrium state representing about 95% transformation of the initial ester as indicated by the chemical equation

$$H_2O + C_2H_5\text{—}O\text{—}CO\text{—}CH_3 \longrightarrow C_2H_5OH + HO\text{—}CO\text{—}CH_3$$

The catalyst acid is unchanged by the reaction and affects both the rate of the forward reaction (hydrolysis) and the backward reaction (esterification).

The best data available are those of Harned and Pfanstiel,[1] who report the coefficients of the rate of reaction calculated as follows: t is the time in minutes elapsed since the beginning of the reaction; E is the initial molality of the ester and A the initial molality of water; X is the molality of ester transformed at the time, t; K_9 is the coefficient of the rate of hydrolysis and K_9' is the coefficient of esterification; (HCl) is the molality of the catalyst acid.

$$dX/dt = (\mathrm{HCl})\ K_9\ (E - X)\ (A - X) - K_0^{r}\ (\mathrm{HCl})\ X^2$$

The ratio of K_9'/K_9 was taken as 4, the value determined by Berthollet for the ratio $(E - X)(A - X)/X^2$ at equilibrium. Therefore, this equation was simplified by substitution of $4K_9$ for K_9', as follows

$$dX/dt = K_9\ (\mathrm{HCl})\ [(E - X)\ (A - X) - 4X^2] \tag{9}$$

In the data to be discussed, the variations in the term $(A - X)$ are within the apparent error of experiment (1%), so that the success of Equation 9 in describing the results of a given experiment is no indication that this term represents a real factor as has been pointed out by Worley.[3] It seems best to omit it'' until positive evidence for its adoption is found. The equation for the reaction is therefore

$$dX/dt = K_{10}\ (\mathrm{HCl})\ [(E - X) - K_{10}'\ X^2]$$

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[3] Worley, Proc. Roy. *Soc.* (London), 87, 885 (1912). (a) Obviously, although the ions of water are ultimately consumed in the reaction, it does not follow that water is an active agent of the slowest stage which is the stage measured. See Scatchard, THIS JOURNAL, 43, 2406 (1921), for an important effort to correlate the activity of water with variations of K_{obs}. in sucrose hydrolysis.

From the data of Harned and Pfanstiel K_{10}' is found to equal 0.068 K_{10}. Therefore the equation may be rewritten as follows

$$dX/dt = K_{10}\,(\mathrm{HCl})\,[(E - X) - 0.068\,X^2] \qquad (10)$$

In this expression K_{10} is the coefficient of the hydrolysis calculated on the assumption that water is not an active agent of the reaction measured. The other terms have the meaning already assigned.

Equation 10 may be integrated after substitution as follows

Let $f = 0.068$ and $g = \sqrt{4Ef + 1}$: then

$$(\mathrm{HCl})K_{10} = (2.303/gt)\log_{10}(g\ 4\ 2fX + 1)(g - 1)/(g - 2fX - 1)(g + 1)$$

In Table I are given the details of an experiment reported by Harned and Pfanstiel.[1] The column headings are self explanatory. It will be seen that since $(\mathrm{HCl})K_{10}$ has the same order of constancy as $(\mathrm{HCl})K_9$, Equation 10 describes the rate of reaction in question just as satisfactorily as Equation 9.

TABLE I

HYDROLYSIS OF ETHYL ACETATE IN 0.20 MOLAL AQUEOUS HYDROCHLORIC ACID SOLUTION AT 25°

Data of Harned and Pfanstiel[1]

$E = 0.4724$ Molal $g = 1.0623$ $f = 0.068$ (HCl) = 0.20 Molal

X	Time, minutes	$(\mathrm{HCl})\,K_9 \times 10^6$	$(\mathrm{HCl})\,K_{10} \times 10^3$
0.000	0	...	...
.06433	119	2.345	1.232
.1058	206	2.345	1.231
.1486	307	2.337	1.231
.1895	419	2.347	1.226
.2283	539	2.335	1.227
.2676	686	2.335	1.227
.3102	885	2.338	1.223
.3406	1058	2.353	1.230
	Average	2.341	1.228

The difference between the lowest and the highest values of coefficients in either series is 0.5%.

In Cols. 1 and 2, Table II, are given the data of an extended series of experiments of Harned and Pfanstiel. From these data, for each experiment represented, the values of X for selected intervals of time were calculated and to these data Equation 10 was applied. The values of K_{10} found appear in Col. 3 of Table II.[4]

Cols. 4 and 5 contain γ'_{HCl} and γ_{KOH} taken from the data of Scatchard[5] and of Harned,[6] respectively.

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[4] Reference should be made to the Harned and Pfanstiel paper (ref. 1) for the equation for calculation of the values of X. In brief, the equation used was

$$K_9\,(\mathrm{HCl}) = \frac{0.04117}{t}\log\frac{(-2.738 - 0.1506X)}{(-2.738 + 6X)}$$

[5] Scatchard, THIS JOURNAL, 47, 641 (1925).

[6] Harned, *ibid.*, 47, 682 (1925).

TABLE II

COEFFICIENTS OF THE RATE OF HYDROLYSIS OF ETHYL ACETATE: IN SOLUTIONS OF VARYING HYDROCHLORIC ACID MOLALITY AT 25°[1]

Molality of ester, 0.47

HCl, molality	$K_9 \times 10^6$ (ref 1)	$K_{10} \times 10^3$ or $K_{obs} \times 10^3$	γ'_{HCl} (ref 5)	γ_{KOH} (ref. 6)	$K_0'd \times 10^3$ (see Equation 7)
0.010	1.167	**6.19**	0.910	0.920	**6.26,**
.030	1.147	6.03	.860	.857	6.01
.050	1.146	6.02	.836	.820	5.96
.070	1.139	5.99	.817	.800	6.03
.100	1.146	6.01	.801	.789	5.92
.150	1.157	6.09	.787	.774	5.99
.200	1.164	6.15	.774	.763	6.06
.300	1.178	6.20	.763	.746	6.06
.500	1.201	6.30	.763	.732	6.04
.700	1.229	6.47	.778	.737	6.13
1.000	1.252	6.58	.817	.760	6.12
1.500	1.307	6.87	.905	.819	6.20

Average of all = 6.06
Average of 1st 6 values of $K_0'd$ = 6.02
Average of 2nd 6 values of $K_0'd$ = 6.10
Difference between 1st and 2nd 6 values of $K_0'd$ = 1.3%

In Col. 6 is the product $K_{10}\gamma_{KOH}/\gamma'_{HCl}$, or $K_{obs.}\gamma_{KOH}/\gamma'_{HCl} = K_0'd$ of Equation 7. The constancy of the product over a variation of acid molality from 0.01 to 1.50 is remarkable. The average of the first six values differs from the average of the last six by only 1.3%.

Hydrolysis of Ethyl Acetate by Hydrochloric Acid in the Presence of Either Potassium or Sodium Chloride.—Harned[7] reports a summary of his own and Taylor's data[8] on the effect of potassium and sodium chlorides on the rate of hydrolysis of ethyl acetate when catalyzed by hydrochloric acid in aqueous solution at 25°. These data are given in Table III.

Both Taylor and Harned calculated the rate of hydrolysis on the assumption that the reaction was complete. The integrated equation used by them in calculating the coefficient, K_{11}(HCl), of the reaction follows

$$(\text{HCl})K_{11} = [1/(t_2 - t_1)] \log_{10} [(E - X_1)/(E - X_2)] \qquad (11)$$

In this expression the symbols are used in the sense already defined except that formula weights per liter are implied instead of molality.

The data for sodium chloride solutions have been included since it seemed probable that at least over a moderate range the activity of the chloride ion in a solution of hydrochloric acid and sodium chloride might be taken as close to that of sodium ion in a solution of sodium hydroxide of like molality to the hydrochloric acid and of like molality of sodium chloride to that of the sodium chloride in the hydrochloric acid solution. Thus

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[7] Harned, THIS JOURNAL, 40, 1461 (1918).

[8] Taylor, *Medd. Vetenskapsakad. Nobelinst.*, 2, No. 34 (1913); also THIS JOURNAL, 37, 551 (1915).

K_0d should be equal to $K_{\text{obs.}} \times \gamma_{\text{NaOH}}/\gamma'_{\text{HCl}}$ if the latter terms are determined in solutions of the same molality of sodium chloride as that used in the catalysis experiments.

The electrolyte composition of the solutions was put in terms of molality on the basis of calculations made from the density data of Ruby and Kawai.[9] No account could be taken in these calculations of the ester in the mixture, as suitable data were not given by the authors. It will be assumed that this error appears consistently in all the results of Table III.

Since the molality of hydrochloric acid was found to have changed slightly from one experiment to the other, a proportionate correction was applied to K_{11} in order to have the results refer to a solution of **0.1005** molality. These coefficients appear as $(\text{HCl})K_{11}'$ in Col. 5, Table III. In this table values of γ'_{HCl}[10] and of γ_{KOH}[11a] and of γ_{NaOH}[11b] are taken from the work of Harned. Col. 8 gives the product $K_{11}'\gamma_{\text{KOH}}/\gamma'_{\text{HCl}}$, which is the same as $K_{\text{obs.}}\gamma_{\text{KOH}}/\gamma'_{\text{HCl}} = K_0'd$ of Equation 7. The absolute value of K_0d ($288 \times 10^{-5} \times$ **2.303** = **6.67** $\times 10^{-3}$) is not the same as that of Table II, which is 5.92×10^{-3}. A small part of the difference may be accounted for by the neglect of the presence of the ester already referred to. However, the main part of the difference must be due to some consistent difference of experimental conditions. The slight irregularity of the values is within the probable limits of experimental error. For concentrations up to 1 N, the agreement is close. For greater concentrations a slight increase is found in the potassium chloride experiments and a slight decrease in the sodium chloride series.

TABLE III

EFFECT OF NEUTRAL SALTS ON HYDROLYSIS OF ETHYL ACETATE IN $M/10$ HCl AT 25°

Normality of salt (KCl)	$K_{11} \times$ (HCl) $\times 10^5$ Harned,[7] Taylor[8]	Molality of salt (KCl)	Molality of acid	$K_{11}' \times 10^5$ ($K_{\text{obs.}}$)	γ_{HCl}[10]	γ_{KOH}[11a]	Ko'd $\times 10^6$	Difference from 288 $\times 10^5$, %
0.00	28.8	0.00	0.1005	288	0.79	0.789	288	...
.50	31.45	.51	.1020	309.8	.716	.666	288	0.0
1.00	34.3	1.04	.1040	331.4	.725	.645	295	2.5
1.50	36.6	1.58	.1050	350.1	.750	.644	301	4.5
2.00	39.2	2.12	.1060	371.6	.793	.645	302	5.0
(NaCl)		(NaCl)				γ_{NaOH}[11b]		
0.50	31.75	0.50	0.1005	318	0.741	0.660	283	−2.0
1.00	35.9	1.02	.1020	354	.783	.636	288	0.0
1.50	39.3	1.56	.1040	379	.855	.625	279	−3.0
2.00	42.85	2.09	.1045	411	.944	.620	270	−6.6

Since Taylor[8] has shown that the change in reaction coefficient which is brought about on the addition of salt to a hydrochloric acid solution

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[9] Ruby and Kawai, THIS JOURNAL, 48, 1119 (1926).

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

[11] (a) Harned, *ibid.*, 47, 689 (1925); (b) ibid., p. 684.

of an ester is the same for a variety of esters, the fact that $K_0'd$ is virtually a constant value is proof that the correlation of the influence of the acid as a catalyst with its activity as an acid given in Equation 7 may be considered representative of all hydrolyses of all esters in aqueous hydrochloric acid solution, provided, of course, the ester molality is small so that no material change in the dielectric of the medium is brought about.[12]

Hydrolysis of Sucrose in Hydrochloric Acid Solution.—If $K_0'd$ is calculated for hydrolysis of sucrose on the basis of the data of Fales and Morrell,[13] it is found to be far from constant. Thus for experiments in which the molality of hydrochloric acid is 1.2 $K_0'd$ is *46%* greater than that for 0.1 *M* hydrochloric acid experiments.

Palmaer,[14] years ago, showed that whereas the influence of hydrochloric acid on ester hydrolysis is nearly proportional to its concentration up to tenth normal value, the same is true of sucrose hydrolysis only up to one hundredth normality. This apparently greater catalytic influence of hydrochloric acid in the case of sucrose has been ascribed to an increase in thermodynamic activity of hydrochloric acid brought about by the presence of the sugar.[15]

However, Coppadoro[16] and Griffith, Lamble and Lewis[17] have reported that ester hydrolysis catalyzed by hydrochloric acid takes place at the same rate whether sucrose is present or not, provided that the molalities of the acid and ester are the same in each experiment. Furthermore, Caldwell[18] has shown that for solutions of sucrose varying in molality from 0.25 to 1 and catalyzed by 1 M hydrochloric acid, the coefficient $K_{\text{obs.}}$ is constant within 3%. This could hardly be true if sucrose increases the influence of hydrochloric acid as catalyst.

It seems improbable, therefore, that the difference in result in the two reactions is due primarily, at least, to a change in behavior of acid but rather to some other variable not yet defined. The greater complexity of the sucrose molecule suggests that more than one catalyst group may be active.[19] The point important to this discussion is that from the failure

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[12] See Harned and Fleysher, THIS JOURNAL, 47, *82 (1925)*; Scatchard, *ibid.*, 47, *2098 (1925)*; Lucasse, *ibid.*, 48, *626* (1926), for examples of the effect of non-electrolytes on the activity of hydrochloric acid in aqueous solution.

[13] Fales and Morrell, *ibid.*, 44, *2021 (1922)*.

[14] Palmaer, *Z. physik. Chem.*, 22, *492 (1897)*.

[15] Jones and W. C. McC. Lewis, *J. Chem. Soc.*, 117, *1123 (1920)*. See also ref. 13 and Scatchard, THIS JOURNAL, *48, 2026* (1926).

[16] Coppadoro, *Gazz. chim. ital.*, *31, I, 425 (1901)*.

[17] Griffith, Lamble and Lewis, *J. Chem. Soc.*, 111, *389* (1917).

[18] Caldwell, *Proc. Roy. Soc. (London)*, 78A, *272 (1906)*.

[19] *In* a forthcoming paper it will be demonstrated that

$$K_{\text{obs.}} = A(\gamma_{\text{HCl}}/\gamma_{\text{KOH}}) + B(\gamma_{\text{HCl}}^2)\,[\text{HCl} + \text{KCl}]$$

In this expression A and B are constants characteristic of the temperature at which measurements are made. (E. M. T., February, 1928.)

of Equation 7 to describe the results of sucrose hydrolysis we may not yet conclude that the success of this equation with other reactions is purely an empirical matter.

Summary of Results on Catalysis by Hydrochloric Acid.—The constancy of $K_0'd$ calculated by means of Equation 7 has been established for the hydrolysis of esters in the presence of hydrochloric acid and potassium or sodium chloride over a very considerable variation of molality. It is of interest that Taylor and Close[20] report the variation of catalytic power of hydrochloric acid with changing molality or with the addition of neutral salts in the case of the formation of valerolactone from hydroxyvaleric acid is parallel to the variation of activity of hydrochloric acid under the same conditions in the ease of ester hydrolysis. It is true that there is much similarity between ester hydrolysis and lactone formation in that it is probable that both depend on the formation of intermediate oxonium compounds.[21] However, they represent the simplest cases of catalysis and should be taken as the basis of study of this obscure subject.

Equation 7 does not describe the results of sucrose hydrolysis. However, this reaction is more complex than the above type and it is to be anticipated that it may be interpreted in the light of the success gained with the simpler cases.

The Catalytic Activity of Potassium Hydroxide and of Sodium Hydroxide.—The most extensive data on the catalytic influence of potassium hydroxide and sodium hydroxide are those of Åkerlöf[22] on the decomposition of diacetone alcohol to form acetone

$$CH_3—CO—CH_2—CHOH—(CH_3) \longrightarrow 2CH_3—CO—CH_3$$

In aqueous solution the change may be considered complete and for a given molality of catalyst a coefficient of the reaction may be calculated by application of the well known equation for a monomolecular change to the variation of the volume of the solution. Neither initial nor final material binds an appreciable part of the catalyst.

Table IV presents the data of Åkerlöf on the rate of this reaction in the presence of tenth molal potassium hydroxide in potassium chloride of varying molality up to 2. The final column gives K_0d and it is seen to be a truly constant term.[23]

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[20] Taylor and Close, THIS JOURNAL, 39, 422 (1917); Taylor and Wilberforce, *J. Phys. Chem.*, 29, 1085 (1922).

$K_0'd$ calculated for their data is constant to 2+% for molalities of KCl up to 0.5. They report one other value and this is for unit molality of KCl from which a value of K_0d is found which is 7% higher than the average of others.

[21] (a) Stieglitz, *Int. Comg. Arts Sci.*, 4,276 (1904); (b) *Am. Chem. J.*, 39, 181 (1907); (c) Kendall and Booge, THIS JOURNAL, 38,1713 (1916).

[22] Åkerlöf, THIS JOURNAL, 48,3046 (1926); see also ref. 23.

[23] Since the presentation of this paper, February, 1927, Dr. Åkerlöf has published

The data for sodium hydroxide catalysis of the reaction in question are not so regular; values of K_0d calculated for 0.0, 0.5, 1.0, 1.5 and 2 molal sodium chloride, respectively, with tenth molal sodium hydroxide are 0.202, 0.189, 0.186, 0.186, 0.186. The variation of K_0d is a matter of 8%.

TABLE IV

APPLICATION OF EQUATION 8 TO DATA OF ÅKERLÖF ON THE DECOMPOSITION OF ACETONE ALCOHOL[1] AT 25° IN SOLUTIONS OF 0.1 M POTASSIUM HYDROXIDE AND VARYING POTASSIUM CHLORIDE MOLALITY

KCl molality	γ_{KOH}[13]	γ'_{HCl}[12]	$K_{obs.}$	K_0d
0.00	0.789	0.79	0.204	0.204
.50	.666	.74	.183	.204
1.00	.643	.78	.166	.201
1.50	.644	845	.153	.201
2.00	.645	.93	.142	.205
			Average	.203

Widest deviation from the average, 1%.

Elsewhere[24] it is shown that Equation 8 applies accurately to the data of hydrolysis of ethyl acetate in hundredth molal sodium hydroxide in the presence of sodium chloride up to half molality (the extent of the measurement).

The alkaline hydrolysis of sucrose is not being considered in this paper as it is still more complex than the acid hydrolysis. For example, Cohen[25] has shown that sucrose binds no small portion of the catalyst base. The decomposition of nitrosotri-acetone-amine to form phorone and nitrogen is also not considered since Francis and co-workers,[26] who have made the measurements on this reaction, report it complex and the true nature of all the products unknown.

Summary of Results on the Catalytic Activity of Potassium Hydroxide and Sodium Hydroxide.—In dilute solutions of sodium or potassium hydroxide, hundredth to tenth molal for example, it is usually found[27] that the coefficient of the catalyzed reaction $K_{obs.}$ is constant. During this interval the ratio $\gamma_{KOH}/\gamma'_{HCl}$ is very nearly equal to 1 so that the application of Equation 8 to the data is successful. A severe test is made, however, when Equation 8 is applied to the data of Åkerlöf in which

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further results of measurements on this reaction in more concentrated potassium hydroxide solutions. Since he does not assure us that the products are the same as in the dilute solution reactions, the interpretation of the results is in doubt. Nevertheless, it is of interest that K_0d proves to be constant for molalities of KOH up to 1.0. See THIS JOURNAL, 49, 2955 (1927).

[24] Wilson and Terry, THIS JOURNAL, 50, 1250 (1928).

[25] Cohen, *Z. physik. Chem.*, 37, 68 (1901).

[26] Francis and Clibbens, *J. Chem. Soc.*, 101, 2358 (1912); Francis and Geake, ibid., 103, 1722 (1913).

[27] See for example ref. 24; also the work of Koelichin, *Z. physik. Chem.*, 33, 129 (1900), on the decomposition of acetone alcohol in dilute aqueous alkali.

the molality of the salt, potassium chloride, varied from 0 to 2.0 and the two γ terms change in a quite different manner. The data of Wilson and Terry also furnish a convincing test that Equation 8 does formulate the real variables of experiment.

The Catalytic Activity Coefficients of Hydrochloric Acid, Potassium Hydroxide and Sodium Hydroxide.—Since each of the terms $\gamma'_{HCl}/\gamma_{KOH}$, $\gamma_{KOH}/\gamma'_{HCl}$ and $\gamma_{NaOH}/\gamma'_{HCl}$ multiplied by the molality of the catalyst to which they respectively refer describes the activity of that catalyst as measured by its influence on the rate of the reaction in question, these terms may be properly called the catalytic activity coefficients of hydrochloric acid, potassium hydroxide and sodium hydroxide. The formulation of these coefficients in terms of experimental data secured from measurements other than those of the rate of the reactions catalyzed is new and their correctness is an experimental fact.

Discussion of Results.—The very considerable breadth of application of Equations 7 and 8 warrants a brief discussion of the possible validity of their derivations and an expression of opinion as to the nature of the d term.

At the outset it must be remembered that we have no insight into the mechanism of the reactions in question other than that given by the successful formulation of equations describing the rate of change. That an equation should be broadly successful argues that it gives at least a graphic representation of the variables affecting the slowest stage of the reaction. The case of the hydrolysis of sucrose, to which the equation does not apply, makes us aware of a new variable which may have existed in the cases of successful operation of the equation but may have been hidden by other unknown and compensating effects. Therefore, until we have an expression which describes the catalytic activity of hydrochloric acid in sucrose hydrolysis both with and without the presence of salts, there is no certainty that the correctness of the simple assumptions used in the derivation of Equations 7 and 8 is confirmed by the latters' success.

We may, however, weigh the possible meaning of the evidence at present available. Assumptions 1 and 2 have been generally used[28,29] and at present there is no evidence against them. The d term is the obvious basis of speculation. The reciprocal value, $1/d$, is that factor which multiplied by the thermodynamic activity coefficient of the catalyst ion gives the coefficient characteristic of its catalytic behavior (calculated in terms of molality of ion present). The present currently used conception of the independent

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[28] Assumption 1 was first used by MacInnes, THIS JOURNAL, 41, 1086 (1919). He assumed that the activities of potassium and chloride ion at like molalities are the same in neutral and non-neutral solutions. This is not done in the present work.

[29] For an excellent bibliography of recent efforts, see Note 1, p. 3046, of ref. 22.

activities of ions leads to the conclusion that $1/d$ is not a constant. Nevertheless, it should be remembered that this theory of ionic behavior has no direct experimental basis.[30]

The fact that the catalytic activity coefficients of hydrochloric acid and potassium hydroxide are reciprocal values so that their product is unity may seem critical evidence against the idea that d is a constant; for in solutions of potassium chloride (and sodium chloride), the (geometric) average of the activity of coefficients of hydrogen and hydroxide ion have been proved by Harned[31] to vary with the molality of salt present in solution. Obviously either the indicated relation of the activity coefficients of hydrogen and hydroxide ions does not hold completely to zero molality of acid and base or else the new functions are not the thermodynamic activity coefficients of the catalyst ions, The correct choice of these alternatives may not yet be made.

It may therefore be concluded that it is not impossible that d is a constant term, and that the activity of the catalyst is defined by the thermodynamic activity of the catalyst ion. However, not until more extensive evidence is available will this interpretation seem probable.

A totally different interpretation of Equations 7 and 8 would be that of the Bronsted theory[32] which calls for equations of just such form. However, the fact that in many reactions the catalytic activity coefficient of hydrochloric acid is independent of the substance undergoing change is in conflict with this theory.

Summary

Expressions are reported which represent the influence of aqueous hydrochloric acid, potassium hydroxide and sodium hydroxide, respectively, as catalysts at varying molalities. The terms of these expressions are the thermodynamic activity coefficients of the substances named.

It is demonstrated that these expressions describe correctly the catalytic

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[30] This principle has been adopted as the simplest explanation of the experimental fact pointed out by Lewis and Randall, THIS JOURNAL, 43, 1141 (1921), that in dilute solution (about up to 0.02 ionic strength) the activity coefficient of a given electrolyte is determined by (its valence type and) the ionic strength of the solution and is not dependent on the nature of the other ions present in solution. However, as Lewis and Randall point out (ref. 2, p. 380) the deduction from this fact, that the activity coefficient of an ion is likewise independent of the nature of its neighbors, is not a necessary one since "some peculiar compensation" may operate so that though in dilute solution the geometric mean of the activity coefficients of the ions of a given electrolyte is independent of the nature of other ions present in solution, still the activity coefficients of the ions themselves vary. It should be added that these authors believe the second explanation improbable.

[31] Harned, THIS JOURNAL, 47, 930 (1925). Harned's activity coefficient of water is the activity coefficient of ionized water, not the activity coefficient of water calculated from vapor pressure measurements.

[32] Brönsted, *Z. Physik*, 102,169 (1922); 115,337 (1925).

activity of the agents in question even when they function in the presence of neutral salts (potassium and sodium chlorides) in acid and alkaline hydrolysis of esters, and in the decomposition of diacetone alcohol in the presence of potassium hydroxide.

Alternative interpretations of the new expressions are discussed.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

THE EFFECT OF NEUTRAL SALTS ON THE VELOCITY OF SAPONIFICATION OF ETHYL ACETATE BY SODIUM HYDROXIDE. I

BY STANLEY DAVIS WILSON AND ETHEL M. TERRY

RECEIVED JULY 5, 1927 PUBLISHED MAY 5, 1928

The following report[1] contains new data on the effect of sodium chloride, sodium acetate and sodium nitrate respectively on the velocity of saponification of ethyl acetate by sodium hydroxide in water solution at 25.00°.

The technique already reported[2] was used in the measurements except that in part of this work a more convenient apparatus[3] was employed. Important details of the experiments will be found in the second part of this paper.

From the results a coefficient, K_1, was calculated by means of the equation for the rate of a bimolecular change:

$$dX/dt = K_1 [B - X][E - X] \qquad (1)$$

In this expression and elsewhere in this paper, K represents a coefficient defined by the equation, the number of which is indicated by the subscript. The terms B and E are the initial molalities (gram molecular weights per 1000 g. of water) of the sodium hydroxide and ester, respectively. The molality of ester or of sodium hydroxide transformed up to the time, t, is represented by X. The values found for K_1, though constant for any stage of a given reaction, decreased as the molality of salt present at the beginning of the experiment was increased, as shown in Table I. The rate of this decrease proved to be characteristic of the salt used, as was of course expected. The coefficients are reproducible to within a quarter of one per cent. and are accurate to three-fourths of one per cent., as is explained in the preceding paper.[2]

Fundamental Equation for the Reaction.—Elsewhere[4] it has been

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[1] The experimental work of this paper was completed in 1916 and was presented by S. D. Wilson as part of a thesis submitted in fulfilment of part of the requirements for the degree of Doctor of Philosophy at the University of Chicago. See also note of Terry and Stieglitz, Ref. 2.

[2] Terry and Stieglitz, THIS JOURNAL, 49, 2216 (1927).

[3] This will be described in a later paper by Gooch and Terry.

[4] Terry, THIS JOURNAL, 50, 1239 (1928).

TABLE I

SAPONIFICATION OF ETHYL ACETATE BY SODIUM HYDROXIDE IN AQUEOUS SALT SOLUTION

Ester = 0.0080 Molal. NaOH = 0.010 Molal

Experiments on NaCl solutions			Experiments on $NaC_2H_3O_2$ solutions		Experiments on $NaNO_3$ solutions	
Molality of NaCl	K_1	Average K_1	Molality of sodium acetate at start	K_1	Molality of $NaNO_3$	K_1
0.0000		6.76	0.00	6.76	0.00	6.76
.0208	6.68					
.0208	6.70	6.68	0.021	6.71	0.014	6.68
.0209	6.67					
.0200	6.67					
.0350	6.67	6.67	.048	6.65	.049	6.57
.103	6.57	6.57	.093	6.66	.099	6.41
.104	6.57					
.511	6.13	6.13	.505	6.61	.355	5.87
.511	6.13				.502	5.66

shown that the catalytic activity coefficient of potassium hydroxide present in solution with no other electrolyte or in solutions of potassium chloride is the ratio of two terms. The first term is the activity coefficient of potassium hydroxide determined by electromotive force, etc., measurements on solutions of potassium hydroxide or potassium hydroxide and potassium chloride each at the molality present in the reaction mixture. The second term is the activity coefficient of hydrochloric acid at like molality to that of the potassium hydroxide in the reaction mixture and present in a solution of potassium chloride equal in molality to that in the reaction mixture. If A represents the catalytic activity of potassium hydroxide, then it may be represented in the form of an equation, as follows

$$A_{\mathrm{KOH}} = (\gamma_{\mathrm{KOH}}/\gamma_{\mathrm{HCl}})(\mathrm{KOH}) \qquad (2)$$

The gamma terms here, as elsewhere in this paper, represent the activity coefficients of the substances indicated in the subscripts. Gamma terms which appear in the same equation always refer to like molalities of the substances named and are determined under corresponding conditions as stated above. The term (KOH) is the molality of potassium hydroxide in the experiment in question.

It seemed probable that the corresponding expression

$$A_{\mathrm{NaOH}} = (\gamma_{\mathrm{NaOH}}/\gamma_{\mathrm{HCl}})(\mathrm{NaOH}) \qquad (3)$$

would be found to describe the catalytic activity of sodium hydroxide in the saponification of an ester in the dilute solutions used in the present work.

The equation for the reaction, therefore, should be

$$\mathrm{d}X/\mathrm{d}t = K_4\,(\gamma_{\mathrm{NaOH}}/\gamma_{\mathrm{HCl}})(B - X)(E - X) \qquad (4)$$

K_4 is the coefficient of the reaction. The other terms are used in the sense already defined. By comparison of Equation 1 with Equation 4, it is found that

$$K_4 = K_1\,\gamma_{\mathrm{HCl}}/\gamma_{\mathrm{NaOH}} \qquad (5)$$

Since in the reaction in question sodium acetate replaces sodium hydroxide as the reaction progresses, it is proper to consider the activity coefficient of sodium hydroxide constant and equal to that of the initial sodium hydroxide. Since the solutions are dilute[6] this assumption is a close approximation to the truth so that the uncertainty of the activity coefficients is not greater than 1%.

The activity coefficients of sodium hydroxide and hydrochloric acid in solutions of one one-hundredth molality and varying molality of sodium chloride have been supplied by Harned.[6]

These are given in the unbracketed values of columns in Table II.

TABLE II

APPLICATION OF EQUATIONS 4 AND 5 TO THE DATA FOR SODIUM CHLORIDE (TABLE I)

(Bracketed data are extrapolated)

Molality of NaCl	K_1	γ_{HCl} (0.01 Molal)[6b,7]	γ_{NaOH} (0.01 Molal)[6a]	K_4
0.00	6.76	0.91	0.92	6.69
.021	6.68	[.86]	.847	6.78
.035	6.67	[.84]	.817	6.85
.104	6.57	.784	.758	6.81
.511	6.13	.729	.661	6.81
			Average,	6.79

The bracketed values of γ_{HCl} are taken from the data of Scatchard[7] and are the activity coefficients of hydrochloric acid at molalities equal to that of the sodium chloride plus one one-hundredth. This interpolation of the activity coefficients of the reagents in these dilute solutions is correct to within 1%, since a comparison of the interpolated and observed values for tenth molal solutions of salt and 0.01 molal acid or base gives agreement to 1%.

The constancy of the values of K_4 is apparent from an inspection of Col. 5, Table II. The average value is 6.79 and the widest deviation from the mean is 1.5%.

Therefore, Equation 4 describes correctly the rate of saponification of ethyl acetate in dilute sodium hydroxide and chloride solution. Possible interpretations of this equation are discussed elsewhere.[4]

Suitable activity coefficients are lacking for an interpretation of the data for reactions in which sodium acetate and sodium nitrate are present.

Part II. Details of Experiments

As has been stated, the general method of procedure was much the same as that employed by Terry and Stieglitz.[2] In addition, the following points should be mentioned.

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[5] See Lewis and Randall's discussion of this subject, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 367.

[6] (a) Harned, THIS JOURNAL, 47, 684 (1925); (b) 48, 326 (1926).

[7] Scatchard, *ibid.*, 47, 645 (1925).

The ester used was prepared exclusively by the Wade and Merriman[8] method, as this was found to be the most efficient.

Soda lime used in purifying air for solution containers was prepared by the method of Atwater and Benedict.[9] It always contained traces of iron from the vessels used in its preparation and it is interesting that Guareschi[10] reports that such a product is more efficient than soda lime made from pure materials.

Sodium chloride and sodium nitrate solutions were made from dried samples of the c. p. salts. The sodium acetate solution was made from pure acetic acid and sodium hydroxide. Special precautions were taken to be sure that these solutions were carbon dioxide free. A known amount of the corresponding acid was added to each salt solution and the mixture was aerated with carbon dioxide free air. The salt solutions were then brought to the point of equivalent acid and base by suitable addition of the latter.

In all cases the concentration of salt in the reaction mixture was calculated on the assumption that the total volume of solution equaled the sum of the volumes of water and reagent solutions which had been combined. This involved an error of less than 0.5% in the estimation of the concentration of the salt and was a negligible matter.

As a preliminary to the measurements for sodium hydroxide and ester concentration, it was first necessary to show that a given quantity of hydrochloric acid or acetic acid (such as was used in our samples) would require the same quantity of standard base in the presence of the excess salt (sodium chloride, nitrate or acetate) as in the absence of salt, that is, that the sensitiveness of the indicator, phenolphthalein, was not materially altered by the presence of high concentrations (0.5 N) of salt. No salt effect was found provided titrations were carried out at 0°.

In the case of the acetate solutions, it was necessary to consider whether the results of titration represented correctly the concentration of free base in the reaction mixture. As long as excess sodium hydroxide was present, the salt could be considered non-hydrolyzed. However, as the end-point was approached in titrations, this condition did not hold. In other words, a small quantity of the salt was used up in titration to an end-point of $[H^+] = 10^{-8}$, so that the results of these measurements were a little too high. Corrections were calculated from the usual equation for the hydrolysis of sodium acetate, $K_{\text{hydrolysis}}$ being taken as $0.11 \times 10^{-14}/1.77 \times 10^{-5}$.[11] The correction for half molar sodium acetate mixtures proved to be 0.09 cc. of $M/100$ HCl reagent for each titration value (125 cc. volume), and for tenth molar sodium acetate the correction was 0.02 cc.

Summary

Report is made of determinations of the effect of sodium chloride, sodium acetate and sodium nitrate, respectively, on the rate of saponifi-

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[8] Wade and Merriman, *J. Chem. Soc.*, 101, 2429 (1912).

[9] Atwater and Benedict, *Carnegie Inst. Washington Pub.*, *42*, p. 29.

[10] Guareschi, *C.* A., **10,** 25 (1916).

[11] 0.10×10^{-14}, the ion product of water at 0°, is an average value taken from data given by Landolt-Börnstein, Julius Springer, 1923, p. 1164.

cation of ethyl acetate by sodium hydroxide in aqueous solution. The initial molalities of ester and alkali were (3.008 and 0.01, respectively. The molality of the salt solutions varied from 0.02 to 0.5.

Only in the case of solutions of sodium chloride are suitable activity coefficients available for the interpretation of the results. In these instances it was demonstrated that the rate of the reaction is dependent on the molality of the ester and the catalytic activity of sodium hydroxide calculated by means of the expression corresponding to that which has elsewhere been shown to represent correctly the catalytic activity of potassium hydroxide.

Chicago, Illinois

[Contribution from the Soils Research Laboratory, Alabama Agricultural Experiment Station]

THE ADJUSTMENT OF THE REACTION OF INDICATOR SOLUTIONS AND ITS IMPORTANCE IN DETERMINING THE HYDROGEN ION CONCENTRATION OF SLIGHTLY BUFFERED SOLUTIONS

By W. H. Pierre and J. Franklin Fudge

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Introduction

The determination of the hydrogen ion concentration of slightly buffered solutions has been known to be subject to various sources of errors. It has long been recognized that the hydrogen electrode, as ordinarily used, is unsatisfactory for such solutions. Lately, Beans and Hammett[1] have shown that by taking certain precautions the hydrogen ion concentration of slightly buffered solutions can be determined by the hydrogen electrode, but their electrodes become inactive quickly and the method is not adapted to routine work. Kolthoff and Bosch[2] studied the use of the quinhydrone electrode for such solutions. They found that it can be used with certain modifications for slightly buffered solutions but that it is best suited for use with solutions of moderate buffer capacity. The most generally used method for the determination of the reaction of slightly buffered solutions, however, is the indicator or colorimetric method. It, too, is open to certain objections. The one error most commonly overlooked is probably the reaction of the indicator solutions used. This has recently been emphasized by the work of Stern[3] and of Schlegel and Stueber.[4] During the last few years the writers have observed the importance of this point in working with slightly buffered soil extracts.

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[1] Beans and Hammett, This Journal, 47, 1215 (1925).

[2] Kolthoff and Bosch, *Chem. Weekblad*, 24, 78-80 (1927); *C. A.*, 21, 1586 (1927).

[3] Stern, *J. Biol. Chem.*, 65, 677 (1925).

[4] Schlegel and Stueber, *Ind. Eng. Chem.*, 19, 631 (1927).

It is the purpose of this paper to present data along this line and to describe a simple method for adjusting the reaction of indicator solutions which has been used in this Laboratory for the last two years.

To What Reaction Should Indicator Solutions Be Adjusted?

Before discussing the methods used in preparing indicator solutions, it seems desirable to consider from a theoretical viewpoint the reaction to which the various indicators should be adjusted. In discussing the use of indicators for determining the reaction of unbuffered material, Taylor[6] states "that the indicator solutions should have a neutral reaction, since any excess acid or alkali will likewise change the P_H value of the material." While at first thought it might seem that all indicator solutions should be neutral and that a neutral indicator would not affect the P_H of the solution to be tested, it can readily be proved that such is not the case. If, for example, brom cresol green adjusted to P_H 7.0 is used for the determination of the reaction of an unbuffered solution of P_H 4.5, the indicator will tend to change the reaction of the unbuffered solution toward its own reaction. The resultant P_H reading will be too high, as is shown by the data presented in Table IV.

Michaelis[6] states "that the indicator method can only give correct results if the P_H of the fluid under investigation is not altered by the addition of the indicator." This condition can only be met when the indicator solution has the same or almost the same reaction as that of the unknown. Any given indicator is used over a rather limited P_H range designated by Kolthoff as the transition interval. If, therefore, its reaction is adjusted to a P_H corresponding to the middle of the transition interval, it will be approximately of the same reaction as that of any unknown whose reaction can be determined with that particular indicator. It is obvious, therefore, that instead of adjusting all indicators to neutrality the various indicator solutions should be adjusted to a P_H corresponding to about the middle of the transition interval. These values for the various indicators used by the writers are: Brom phenol blue, 3.80; Brom cresol green, 4.60; Brom cresol purple, 5.80; Brom thymol blue, 6.80; Phenol red, 7.60.

Methods of Preparing Indicator Solutions

Various methods have been used in preparing indicator solutions but little consideration has been given until recently to the adjustment of their reaction. Some of the early workers, Friedenthal,[7] Salm[8] and Sørensen[9] believed that the acidic and basic properties of indicator solu-

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[5] Taylor, "The A B C of Hydrogen Ion Control," LaMotte Chemical Products Company, Baltimore, Maryland, p. 17.

[6] Michaelis, "Practical and Colloid Chemistry," 2nd ed., p. 47.

[7] Friedenthal, *Z. Elektrochem.*. **10**, **113** (1904).

[8] Salm, *Z. physik Chem.*, **10**, **341** *(1904)*; **12**, 99 **(1906)**.

[9] Sørensen, *Biochem. Z.*, **21**, **131** **(1919)**; **22**, **352** **(1919)**.

tions would affect the P_H of unbuffered solutions and, therefore, concluded that the P_H of pure water or solutions of strong acids or base could not be determined by the colorimetric method.

While Kolthoff[10] does not agree fully with this viewpoint, he believes that with some indicators an error may be introduced if their acidic properties are not considered. In the preparation of sulfonephthalein indicators, however, he does not adjust the reaction of the indicator solutions His method of preparation consists in dissolving 100 mg. of indicator in 20 cc. of warm alcohol and diluting to 100 cc. with water.[11]

Probably the most common method of preparing the sulfonephthalein indicators, used largely in this country for P_H work, is that recommended by Clark,[12] in which the theoretical amount of base necessary to form the salt is added. The inadequacy of this method when working with slightly buffered solutions has been shown by Stern and by Schlegel and Stueber, with regard to the use of brom thymol blue indicator.

Both Stern and Schlegel and Stueber tested the neutrality of their brom thymol blue indicator with especially prepared conductivity water of P_H 7.0. The indicator solutions were adjusted by the addition of alkali until the neutral conductivity water tested with the indicators gave a P_H of 7.0. The difficulty of obtaining conductivity water of P_H 7.0, however, is a serious objection to their method. Moreover, the method can only be used when the indicator solution is to be adjusted to P_H 7.0.

Quinhydrone Titration Method.—Stern used the quinhydrone electrode in determining the reaction of his indicator solutions and found that the readings were accurate to within 10 millivolts. Evidently, then, the quinhydrone electrode can be used for the adjustment of the indicator solutions to any desired reaction. It was used by the writers and found very satisfactory. The hydrogen electrode, on the other hand, was found in preliminary work to be unsatisfactory, for a constant potential is not obtained. Apparently this is due to the reducing effect of the hydrogen introduced, for the indicator solutions gradually turn a yellowish-green color as the hydrogen is introduced.

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[10] Kolthoff, "Indicators," John Wiley and Sons, Inc., New York, **1926**, p. 169.

[11] Since this investigation was completed, the attention of the writers has been called to a recent paper by Kolthoff, *Biochem.* Z., **168**, 110-21 (1926), in which the author states that in working with poorly buffered solutions such as distilled water the neutral salts of the indicators should be used since the indicators are acid in character and give erroneous results if not neutralized. He also points out the fact that the sodium salt solution of indicators made up according to Clark may also give slight errors and concludes that when one desires an absolutely accurate result, he must first approximately estimate the P_H of the weakly buffered solution and then use a mixture of the indicator acid with its salt so mixed that the P_H of the mixture approaches that of the solution to be tested.

[12] Clark, "Determination of Hydrogen Ions," 2nd ed., Williams and Wilkins Co., Baltimore, Md., **1923**, p. 80.

The Varying Drop Method.—The method that has been used in this Laboratory for the last two years is based on the principle that if an indicator solution is more acid or more alkaline than the weakly buffered solution to be tested a different hydrogen ion concentration will be obtained when different amounts of the indicator solution are used. The more of the indicator solution added, the more will the indicator have a tendency to change the *PH* of the weakly buffered solution toward its own reaction. It will exert no effect, however, on a strongly buffered solution. Thus, if in comparing the PH of a weakly buffered solution with a standard buffer of the same reaction, 3, 5 and 8 drops of indicator are successively added to each and the unbuffered solution changes its *PH* toward the acid side as compared with the standard buffer, it proves that the indicator solution is more acid than the unbuffered solution. Table I gives an illustration of the results obtained by this method.

Table I

The Hydrogen Ion Concentration of Unbuffered Solutions when Tested with Indicator Solution Variously Adjusted

Indicator	Drops of indicator solution per 5 cc. of solution tested	Hydrogen ion concn. of an unbuffered soln. with indicators adjusted according to	
		Clark, *PH*	Varying drop method. *PH*
Brom thymol blue	3	6.70	6.80
	5	6.40	6.80
	8	6.30	6.80

The unbuffered solution consisted of distilled water to which a little sodium hydroxide had been added. It will be noted that the more of the indicator solution adjusted according to Clark is added, the lower is the PH of the unbuffered solution as compared with the standard buffer. With the indicator solution to which was added more sodium hydroxide the *PH* was the same regardless of whether 3 or 8 drops were used, indicating that the indicator solution had a PH of about 6.80. By thus adding alkali or acid to the indicator solutions until slightly buffered solutions tested with it give the same reaction whether 3 or 8 drops are added, the indicator solutions can be adjusted to the desired *PH*. Although this method is slightly more tedious in operation than is the adjusting of the indicator solution by use of the quinhydrone electrode, it enables one to adjust the reaction of indicator solutions without the use of the electrical apparatus needed for the latter method.

Properties of Indicators Prepared by Various Methods

In order to study the effect of using variously adjusted indicator solutions on the *PH* of unbuffered or slightly buffered solutions, the five common indicators used in soils work were each prepared according to the following methods: (1) solution of indicator acid in alcohol according to Kolthoff,

(2) neutralizing according to the theoretical values recommended by Clark, (3) adjusting the indicators to the P_H values recommended, by means of the varying drop method, and (4) adjustment to P_H 7.0 by titration, using the quinhydrone electrode. In Table II are given the amounts of alkali used in each method and the resulting P_H of the solutions as determined by the quinhydrone electrode. It will be noticed that the indicator solutions prepared according to Kolthoff are very acid and range between P_H 2.51 and 2.80. Adjustment according to Clark also leaves the solutions very acid, varying from P_H 3.73 to 5.19 for the different indicators. It will be seen that the P_H values of the solutions adjusted according to the varying drop method are close to the reaction values previously recommended. It will also be noted that with some indicators it took nearly twice as much alkali to adjust according to the varying drop method as it did according to Clark. Adjustment to P_H 7.0, as would be expected, requires considerably greater amounts.

TABLE II

THE HYDROGEN ION CONCENTRATION OF INDICATOR SOLUTIONS AS ADJUSTED BY VARIOUS METHODS

Indicator	Kolthoff method $N/20$ NaOH, cc.	Kolthoff method H-ion concn., P_H	Clark method $N/20$ NaOH, cc.	Clark method H-ion concn., Pa	Varying drop method $N/20$ NaOH, cc.	Varying drop method H-ion concn.. P_H	$N/20$ NaOH required to adjust to P_H 7.0, cc.
Brom phenol blue	None	2.72	3.0	3.73	3.56	3.96	7.16
Brom cresol green	None	2.80	..	..	3.57	4.53	6.00
Brom cresol purple	None	2.68	3.7	3.76	5.60	5.87	6.80
Brom thymol blue I	None	2.70	3.2	4.97	4.82	7.13	4.60
Brom thymol blue II	...	..	3.2	5.19	4.23	6.78	4.42
Phenol red	None	2.51	5.7	4.29	9.20	7.71	7.98

TABLE III

A COMPARISON OF INDICATORS FROM VARIOUS SOURCES

Indicator	Source	Color of indicator powder	Color of indicator solution made up according to Clark	Color of indicator solution made up according to Varying drop method	Relative tinctorial power
Brom phenol blue	A	Yellowish-orange	Purplish-red	Purplish-red	100
	B	Purplish-brown	Purplish-red	Purplish-red	100
Brom cresol green	A	Yellowish-orange	......	Green	100
	B	Chocolate brown	.....	Green	100
	C	Dark brown	......	Green	98
Brom cresol purple	A	Yellowish-brown	Yellowish-red	Wine red	75
	B	Light pink	Wine red	Wine red	100
	C	Pinkish-yellow	Yellowish-red	Wine red	90
Brom thymol blue	A	Pink	Greenish-brown	Bluish-green	87
	B	Chocolate brown	Greenish-brown	Bluish-green	100
	C	Pink	Greenish-brown	Bluish-green	76
Phenol red	B	Crimson red	Yellow	Red	90
	C	Crimson red	Red	Red	100

A comparison was also made of the properties of indicators secured from different sources. These results are given in Table III. It will be seen that there are marked differences in the appearance of the indicator powders as well as in the color of the indicator solutions made up according to Clark. The color differences of the solutions were found to be related to the hydrogen ion concentration. Thus it was found that the phenol red from source B, which had a yellow color, required 3.5 cc. of $N/20$ sodium hydroxide in excess of that recommended by Clark to bring it to the desired reaction, while that from source C, which was red in color, required only 0.9 cc. Similar variations in the amount of alkali required by indicators from different sources to bring them to the desired reactions were also found for the other indicators.

The relative tinctorial powers of the same indicator from various sources are also given in the last column of Table III. These values were obtained by adding equivalent amounts of each indicator solution to similar amounts of a buffer solution whose P_H was near the middle of the transition interval and by comparing the relative strength of the color produced by means of a colorimeter. It will be noticed that there are marked differences in tinctorial power, which fact emphasizes the importance of using the same lot of indicator in making up solutions to be used for the standard buffers and the unknown solutions.

Errors Due to Method of Preparation or Reaction of Indicator Solutions

Soil extracts were prepared according to the collodion sac method,[13] and their hydrogen ion concentrations determined by using varying amounts of the variously adjusted indicator solutions. The hydrogen ion concentration of the soil suspensions was also determined by means of the hydrogen electrode. The data are reported in Table IV.

It will be noted that the P_H values obtained by the colorimetric method varied greatly depending on how the reaction of the indicators had been adjusted and on the number of drops of indicators added. In all cases there was no difference in the P_H values obtained when different amounts of the indicator solutions adjusted according to the varying drop method were used, but a considerable difference when an indicator solution adjusted according to the other methods was employed. As would be expected, the greater the difference between the reaction of the indicator solutions and that of the solution to be tested, the greater is the error; and the more improperly adjusted indicator solutions used, the greater is the error with these slightly buffered solutions.

The amount of indicator usually recommended is about 10 drops per 10 cc. of solution, which corresponds to 5 drops for 5 cc. Since **3** drops have been found sufficient to give good color differences, this amount is rec-

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[13] **Pierre and Parker,** *Soil Science,* **23, 13 (1927).**

TABLE IV

THE HYDROGEN ION CONCENTRATION OF SOIL EXTRACTS AND WEAKLY BUFFERED SOLUTIONS DETERMINED BY THE USE OF INDICATOR SOLUTIONS PREPARED BY VARIOUS METHODS

Extract of soil or slightly buffered soln.	Specific resistance of extract (23–25° C.) ohms	H-ion concn. (H electrode) PH	Indicator		H-ion concn. obtained with indicators variously prepared Methods of adjustment			
			Name	Drops per 5 cc.	Kolthoff,[a] PH	Clark, PH	Varying drop method, PH	Neutrality method, PH
Sandymuck	6195	3.99	BPB	3	3.85	4.05	4.05	4.10
				5	3.85	4.05	4.05	4.15
				8	3.80	4.05	4.05	4.25
Sassafras loam	10,280	4.61	BCG	3	4.45	..	4.60	4.80
				5	4.30	..	4.60	5.00
				8	4.15	..	4.60	5.05
Norfolk sandy loam	38,664	5.60	BCP	3	5.30	5.45	5.60	5.60
				5	5.15	5.45	5.60	5.70
				8	4.95	5.40	5.60	5.75
Greenville sandy loam	23,184	5.89	BCP	3	5.60	5.80	5.85	5.95
				5	5.40	5.75	5.85	6.00
				8	5.20	5.70	5.85	6.05
Norfolk sandy loam (washed)	45,140	5.60	BCP	3	<5.20	5.45	5.60	5.80
				5	<5.20	5.40	5.60	5.85
				8	<5.20	5.30	5.60	5.95
Distilled water	495,000	..	BCP	3	<5.20	5.20	5.60	5.85
				5	<5.20	<5.20	5.60	5.95
				8	<5.20	<5.20	5.60	6.05
Distilled water and NaOH	72,370	..	BTB	3	6.30	6.75	6.90	6.90
				5	<6.20	6.60	6.85	6.90
				8	<6.20	6.55	6.85	6.90

[a] Since the indicator solution made up according to Kolthoff is 2.5 times as concentrated as the others, 1, 3 and 5 drops were used instead of 3, 5 and 8, respectively. Due to the Kolthoff solution being made up in 20% alcohol, however, it took 38 drops as compared with 26 drops of the other solutions to make 1 cc. Therefore, 3 and 5 drops, respectively, are approximately equivalent to 5 and 8 drops, respectively, of the other solutions.

ommended as being less likely to cause errors from the use of unadjusted indicator solutions than would larger amounts. The data also prove definitely that the reaction of all indicators should not be adjusted to PH 7.0 but rather to a PH corresponding to about the middle of the transition interval. It will also be noted that the hydrogen ion concentration of the soil suspension determined with the hydrogen electrode checks well with that obtained by the colorimetric method, using indicators adjusted by the varying drop method.

The Storage of Indicator Solutions

The question as to how long indicator solutions can be stored has been raised by several investigators. Schlegel and Stueber found that the storage of brom thymol blue in ordinary glass bottles renders the solution alkaline due to the solution of alkali from the glass. They also point out that the coating of the inside of the bottles with paraffin may also lead to a change in the reaction of the stored solutions due to the fact that ordinary paraffin has a distinctly acid reaction. By using Pyrex glass bottles these authors found that brom thymol blue solutions showed no changes in reaction even after prolonged periods of storage, provided the bottles were stoppered to exclude air. If, on the other hand, the bottles were frequently opened the indicator solutions were found to become progressively more acid. Both Stern and Kolthoff also found that neutralized indicator solutions turn somewhat acid on standing.

In order to obtain definite data regarding the effect on the hydrogen ion concentration of indicator solutions stored in different kinds of flasks, the following experiment was conducted. The four indicator solutions used in this study were stored in each of the following kinds of flasks: (1) paraffin coated flasks, (2) thoroughly weathered Pyrex flasks and *(3)* thoroughly weathered reagent bottles of ordinary glass. The bottles were weathered by heating in dichromate solution for a period of one hour, after which they were heated with successive portions of distilled water and thoroughly washed. The indicator solutions, the *PH* values of which had been determined, were placed in these bottles and the bottles stoppered. After a period of nine months the PH value of each was again determined. The results are given in Table V.

TABLE V

THE CHANGE IN HYDROGEN ION CONCENTRATION OF INDICATOR SOLUTIONS AFTER A NINE MONTH'S STORAGE IN VARIOUS KINDS OF FLASKS

Indicator	H-ion concn. before storage. PH	H-ion concn. after storage In paraffin coated flasks, PH	 In weathered Pyrex flasks, *PH*	 In weathered reagent bottles of ordinary glass, *PH*
Brom cresol green	4.70	4.59	4.54	7.23
Brom cresol purple	5.50	3.92	4.05	6.51
Brom thymol blue	6.88	6.76	6 59	7 59
Phenol red	7.84	7 44	7.65	7 95

It will be seen that storage in ordinary glass bottles decreases the hydrogen ion concentration of all the solutions materially, due no doubt to the solution of the glass. Storage in Pyrex or paraffined flasks rendered all the solutions more acid. In the case of the solutions of brom cresol green, brom thymol blue and phenol red the change was small, but a large increase in acidity resulted with the brom cresol purple indicator solution. It is also probable, as pointed out by Schlegel and Stueber, that if the flasks had been opened from time to time a greater increase in acidity would have been noted. The importance, then, of determining and adjusting the reaction of indicator solutions stored even in Pyrex bottles becomes evident if these indicators are to be used with slightly buffered solutions. This is especially true with the brom cresol purple indicator solution.

Conclusion

From these data it is evident that in order to obtain accurate results with slightly buffered soil extracts or unbuffered solutions of any kind, the indicator solutions should be adjusted to a hydrogen ion concentration corresponding to a P_H near the middle of the transition interval. While most soil extracts and most of the various kinds of solutions tested by the colorimetric method are well enough buffered not to be affected by the use of indicator solutions made up according to Clark, the proper adjustment of indicator solutions is no doubt of considerable importance in many lines of work where the hydrogen ion concentration of slightly buffered solutions is determined. The old practice, for example, of diluting strongly colored solutions until the color or turbidity no longer interferes, results in slightly buffered solutions which upon testing with unadjusted indicators may give erroneous results. Schlegel and Stueber have shown the importance of properly adjusted indicator solutions for use in sugar refinery practice. Erroneous results would undoubtedly also be obtained in determining the P_H of many natural waters or in P_H control work in water purification.

Regarding the methods of adjustment, two simple methods are available; the varying drop method and the quinhydrone titration method. The latter is very rapid and convenient but requires the electrical apparatus necessary for electrometric determinations. The former, on the other hand, can be used without this equipment, is simple and gives accurate results.

Summary

A critical study was made of the various methods used for preparing and adjusting the reaction of indicator solutions and a simple method, proposed by the authors, is described. The use of the quinhydrone electrode was also found satisfactory for this purpose. Data are presented on the P_H of indicator solutions adjusted by the various methods and on the effect of using such solutions in determining the P_H of weakly buffered soil extracts and other solutions. It is shown that the use of indicator solutions made up without neutralization, of solutions adjusted to P_H 7.0 and of those made up according to Clark give erroneous results with slightly buffered solutions. For such solutions the indicator solutions are shown to require adjustment to a P_H corresponding to that of about the middle of the transition interval.

AUBURN, ALABAMA

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE PREPARATION OF CHLORIDE FREE COLLOIDAL FERRIC OXIDE FROM FERRIC CHLORIDE[1,2]

BY C. HARVEY SORUM

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Introduction

Among the several theories of structure which have been advanced to account for the stability of colloidal ferric oxide is the so-called "complex" or "solution-link" theory. As recently discussed by Dr. Thomas of Columbia University[3] this theory proposes that the ferric oxide micelle is made up of two parts, an insoluble agglomerate consisting of x molecules of Fe_2O_3 and a soluble attachment, a so-called "solution-link," consisting of y molecules of some soluble salt. In the case of colloidal ferric oxide prepared from ferric chloride the ferric chloride serves as the "solution-link." The empirical formula for the resulting micelle would be $x\mathrm{Fe_2O_3}\cdot y\mathrm{FeCl_3}$.

Although Dr. Thomas does not give us the structural picture of his proposed micelle, we can readily visualize it as taking a form somewhat as follows: an insoluble nuclear mass consisting of x molecules of ferric oxide, and attached to this nucleus and radiating from it in all directions, y molecules of ferric chloride. The ferric chloride, being soluble in water, holds the insoluble ferric oxide nucleus in suspension. The $x\mathrm{Fe_2O_3}\cdot y\mathrm{FeCl_3}$ complex ionizes to give $x\mathrm{Fe_2O_3}\cdot y\mathrm{Fe^{+++}}$ ions and $\mathrm{Cl^-}$ ions. This would explain the positive charge on the colloidal particle as well as the various electrical properties associated with that charge.

The basic idea contained in the "solution-link" theory has been applied by numerous investigators,[4] particularly by Pauli and his co-workers[5] and by Wintgen and Löwenthal. They have accurately determined the amount of iron and chlorine in various samples of purified sol and from these analyses have proposed exact formulas for the micelle in each sol. Unfortunately there is no very close agreement among the twenty or thirty formu-

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[1] The substance of this article was included in a paper presented at the Midwest Regional Meeting of the American Chemical Society, University of Chicago, May 27–28, 1927.

[2] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin. All work was carried out under the direction of Professors F. C. Krauskopf and J. H. Walton, to whom the author is deeply and gratefully indebted.

[3] Thomas, *J. Chem. Educ.*, **2**, 323 (1925); Thomas and Freiden, THIS JOURNAL, **45**, 2522 (1923); Thomas and Johnson, *ibid.*, **45**, 2532 (1923).

[4] Weiser, "The Hydrous Oxides," McGraw-Hill Book Co., New York, 1926, p. 47.

[5] (a) Pauli and Walter, *Kolloidchem. Beihefte*, **17**, 256 (1923); (b) Kuhul and Pauli, *ibid.*, **32**, 319 (1925); (c) Pauli and Rogan, *Kolloid.-Z.*, **35**, 131 (1924).

las which they suggest. However, their formulas, even though they may vary widely, all agree in showing that some chloride is always present in colloidal ferric oxide derived from ferric chloride. In this respect their results bear out the conclusion, emphasized by numerous investigators, that the presence of chloride is not accidental but is a very necessary factor for stability.

Granting then, that chlorides are necessary for the stability of colloidal ferric oxide prepared from ferric chloride, the suggestion arises that, perhaps, if dialysis of impure sols were consistently carried to the very extreme limit of completeness, it should be possible to obtain stable colloids of constant iron-chlorine ratio. Such sols would then be the ultimate in ferric oxide stabilized by chloride and their behavior should be quite uniformly reproducible. To prepare such "ultimate" sols, determine their iron-chlorine ratio and study their behavior toward coagulating agents was the original object of some work undertaken in this Laboratory.

Preparation of the Sol

Four hundred cc. of a molal solution of pure, resublimed ferric chloride was allowed to fall, drop by drop at the rate of two drops per second, into five liters of vigorously boiling distilled water contained in a six liter Pyrex flask. The agitation resulting from the boiling ensured the complete and instantaneous mixing of the ferric chloride solution with the water. Increased temperature increases the rate and degree of hydrolysis, as does removal of the products. As carried out, the ferric chloride contained in a given drop of added solution would be hydrolyzed to the maximum degree before another drop entered the flask. We would thus come very close to having ferric oxide formed in the absence of free ferric chloride. Since increased temperature tends, generally, to decrease adsorption, high temperature hydrolysis should give colloidal ferric oxide with a minimum amount of adsorbed impurity.

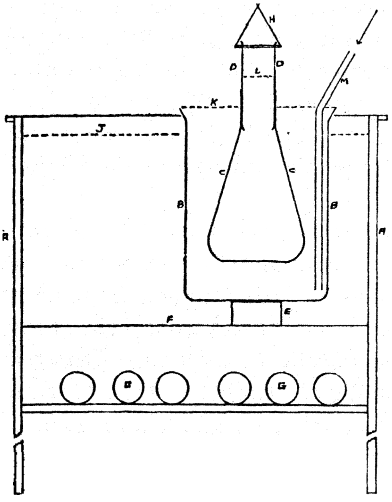

Fig. 1

Purification of the Sol

A slight modification of the continuous method of hot dialysis, as first carried out by Neidle,[6] was employed. The dialyzer (see Fig. 1) consisted of a battery of twelve tall liter Pyrex beakers placed in a steam-heated water-bath the temperature of which was maintained at from 90 to 97°. Pure distilled water was allowed to flow through these beakers at the rate of about three liters per hour, an individual water tap being provided for each beaker. The distilled water was led in at the bottom of the beaker and allowed to overflow at the top, the overflow running into the water-bath and, finally, into the sewer drain. In each of these beakers was suspended a 250cc. collodion

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[6] Neidle, THIS JOURNAL, 38, 1270 (1916).

bag containing impure sol, the bags being attached to two parallel lengths of one-inch glass tubing by means of copper wires fixed to the tops of the glass necks, D. The position of the suspended bag was so adjusted that the level of the overflowing liquid in the beaker was about one fourth of an inch above the bottom of the glass neck to which the bag was attached.

Dialysis was allowed to proceed continuously in the manner indicated and at the above mentioned temperature for periods varying from seven to twelve days. Before removal the contents of each collodion bag was tested for chloride in a manner to be explained later. In every case where dialysis was carried out for a week or more negative tests for chloride were obtained. Contrary to apparently unanimous results obtained by past workers[7] extreme dialysis, even when continued for five weeks at 90–97°, did not induce coagulation.[8]

The purified sols were deeply wine colored, clear to transmitted light, gave a strong Tyndall cone and showed no signs of precipitation even after twelve months The iron content varied from 2.07 to 3.60 g. per liter.

Discussion

The negative chloride tests mentioned above were entirely unanticipated and, in the face of an enormous amount of contrary evidence submitted by other investigators, certainly not to be expected. The probability of error immediately suggested itself, but the results were checked and rechecked, eighty-four independent samples of sol agreeing in giving negative chloride tests. The methods used in testing for chloride were as follows:

1. Twenty-five cc. of chloride free, concentrated nitric acid was added to 50 cc. of sol contained in a 250cc. Pyrex Erlenmeyer flask and set away at room temperature until all ferric oxide had dissolved to give a clear yellow solution of ferric nitrate. Five cc. of a saturated solution of silver nitrate was then added.

2. Twenty-five cc. of chloride free nitric acid was added to 50 cc. of sol contained in a flask. The contents were then warmed on the hot plate until all ferric oxide had dissolved, cooled and treated with 5 cc. of a saturated silver nitrate solution.

3 and 4. Methods 1 and 2 were repeated, sulfuric acid and silver sulfate being used in place of nitric acid and silver nitrate.

5. Method 2 was repeated, the nitric acid and silver nitrate both being added before the flask was heated.

6. Twenty-five cc. of concentrated sulfuric acid and 50 cc. of sol were placed in an all-glass retort, the contents of which were then heated to boiling. The distillate was collected in a cooled flask containing 5 cc. of a saturated solution of silver nitrate.

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[7] Freundlich, "Colloid and Capillary Chemistry," Methuen and Co., Ltd., London, 1926, p. 374.

[8] A private communication from Dr. H. R. Kruyt, University of Utrecht, confirms the fact that extreme dialysis may not always induce coagulation. He reports that prolonged dialysis of sols in his laboratory did not result in their coagulation.

7. A liter of sol was evaporated to 48 cc. and tested as in Method 4.

In each of the seven methods outlined, absence of turbidity after twelve hours was taken as evidence of absence of chloride.

Since the silver nitrate test is recognized to be an excellent test for chlorides, sensitive enough to be used in gravimetric analysis and nephelometry, the validity of the results obtained seemed beyond question. However, there remained the possibility that ferric ion could interfere. Any doubt on that score was, we feel, cleared up in the following manner.

The addition of one drop of 0.00931 N hydrochloric acid to 80cc. portions of the solutions which had given negative tests for chloride when treated according to the seven methods already outlined, gave a distinct turbidity, the addition of two drops gave a pronounced turbidity. The chloride was added as ferric chloride instead of hydrochloric acid, and the same results were obtained. Sols that were dialyzed for only three or four days gave positive turbidity tests, thus showing that chlorides, if present, would not evade detection. The average volume of the drops of 0.00931 N hydrochloric acid added was 0.04 cc. This means that the silver nitrate test, as carried out, is sensitive enough to detect the presence of 0.0000134 g. of hydrochloric acid per 80 cc. of solution, or 0.0001692 g. of hydrochloric acid per liter. The chloride content of the sols prepared, calculated as hydrochloric acid, must, therefore, have been less than 0.0001692 g. per liter.

If from among the twenty or thirty formulas for colloidal ferric oxide suggested by Pauli and his co-workers" we select an average one, say, 60.5 Fe $(OH)_3 \cdot 5FeOCl \cdot FeO^+/Cl^-$, we find that its Fe/Cl ratio is 3713.36/213. The most dilute sol prepared in the course of our study contained 2.07 g. of iron per liter. On the basis of Pauli's formula the chlorine content of such a sol should be 0.119 g. per liter. This is more than seven hundred times as much chlorine as can be detected by the silver nitrate test. We could divide and subdivide this value several times and still be within the limits of its sensitivity.

As such, the results indicate that the ferric oxide micelle, obtained by the hydrolysis of ferric chloride, is not a chlorine complex, a definite chloride compound. We would not venture the conclusion that the sols prepared were absolutely free from all Cl^- ions. There may be, and probably is, a slight trace of chloride present. However, this "trace," as shown by our sensitivity tests, must be less than 0.0001692 g. of hydrochloric acid per liter; and it hardly seems possible that such a small amount of electrolyte can be responsible for stability.

The suggestion arises that we may be dealing with a case of selective adsorption, that some other more readily adsorbable ion, nitrate for instance, may have completely ousted and replaced the chloride ion. However, no nitrate could be detected. To guard against any possible electrolyte contamination, immaculate cleanliness was always observed. The collodion bags used in dialysis were always thoroughly rinsed with distilled water before being put into use. All glassware was steamed and rinsed.

A subsequent paper will deal with the properties of chloride free ferric oxide hydrosols.

Summary

Stable ferric oxide hydrosols giving no test for chloride have been prepared by hydrolysis and hot dialysis of ferric chloride.

MADISON, WISCONSIN

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

THE RELATION BETWEEN THE HYDROLYSIS EQUILIBRIUM CONSTANT OF ESTERS AND THE STRENGTHS OF THE CORRESPONDING ACIDS

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The relationship has previously been mentioned[1] in comparing esters with mixed acid anhydrides, that esters of stronger acids are in general more completely hydrolyzed under like conditions than the esters of weaker acids. This generalization was based upon rather limited and in some cases questionable data, and it was therefore hoped to test out the generalization by obtaining more data on the hydrolysis equilibrium constants of esters of different acids.

It was planned to determine the equilibrium constants by the simple, direct method of heating the acid and alcohol together until equilibrium was established and analyzing the original and final mixtures. Unfortunately experimental difficulties prevented the determination of very many values by this direct method. The reactions are so slow even at 100° that it is necessary in order to reach equilibrium within any reasonable time to have a fairly high concentration of acid to act as catalyst in the final equilibrium mixture. Especially is this true in case a weak acid is being used. One of the principal difficulties introduced by reason of this fact is that of obtaining a homogeneous solution at equilibrium. In many cases sufficient acid for the catalysis will not remain dissolved. Another more or less obvious difficulty limiting the application of this direct method is the fact that "side reactions" are likely to occur. Many acids, for example, decompose under the conditions used before equilibrium in the esterification reaction is attained.

In spite of the fact that the work was not extended as far as it was at first hoped, some data contributing to the question were obtained and are here reported.

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[1] Williams and Truesdail, THIS JOURNAL, 45, 1348 (1923).

Experimental Results and Discussion

Ethyl Esters of Halogen Acids.—Hydriodic acid is the strongest of the halogen acids, hydrobromic acid is next and hydrochloric acid is not as strong as the other two as determined by the ordinary methods. It was accordingly thought desirable to determine the hydrolysis equilibrium constants of the ethyl esters of these acids. Euler[2] had previously determined the value for the hydrochloric acid ester, using essentially the method we had in mind. However, the formation of ether takes place too readily to allow a satisfactory determination of these constants by this direct method. Ether formation is especially noticeable when alcohol is heated with hydrobromic acid. The results obtained, in so far as they can be relied upon at all, indicate that the hydrolysis equilibrium constants of the three ethyl esters are in the same order as the strengths of the corresponding acids, in accordance with the generalization mentioned above. However, the values which were obtained are subject to errors of unknown magnitude due to ether formation and, therefore, are not recorded here. In order to arrive at the true constants it will probably be necessary to make independent measurements of the rates of hydrolysis and esterification in each case and to compute the constants from these data. We are not prepared at present to carry out these more extensive experiments.

Esters of Fatty Acids.—The only fatty acids which show distinct and consistent differences in their acid strengths at all temperatures at which they have been studied are formic, acetic and propionic acids. They are, therefore, the only ones which could be used to throw light on the problem under consideration. The equilibrium "constants" of the methyl esters of these acids were determined under one set of conditions and the values for the ethyl esters were determined for two different sets of comparable conditions.

TABLE I

ETHYL ESTERS OF FATTY ACIDS

A

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.[a]	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Formic	9.95	6.33	9.95	6.33	400	7.62	0	3.62	1.45	214
Acetic	9.00	3.17	9.00	3.17	0	5.83	0	5 83	.296	1 8
Propionic	7 75	2.77	7.75	2.77	35	5.33	0	4 98	289	1 84

B

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.[a]	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Formic	7.25	2.53	12.50	7.78	0	4 72	0	4.72	.883	
Acetic	7.07	1.81	10.31	5.05	0	526	0	526	.332	
Propionic	711	2.12	824	325	0	499	0	4.99	.294	

[a] The "initial" concentration refers to the molar concentration in the original acid–alcohol mixture before reaction has taken place. The "final" concentration refers to the corresponding value after equilibrium is established.

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[2] Euler, *Z physik. Chem.*, 36,405 (1901).

In the experiments summarized in Table IA, equimolecular quantities of the concentrated acid and absolute alcohol were heated together in a boiling water-bath in sealed glass tubes filled nearly full with the mixture, allowing only for thermal expansion. A sample tube was removed from time to time, cooled to 0° and portions titrated with standard alkali. The pipets used were calibrated for this purpose. When the titrations of successive samples became practically constant, it was assumed that equilibrium had been reached.

TABLE II

METHYL ESTERS OF FATTY ACIDS

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Formic	7.10	1.98	18.81	13.69	0	5.12	0	5.12	1.03	21.4
Acetic	7.05	0.93	15.1	8.98	0	6.12	0	6.12	.224	1.8
Propionic	7.11	1.20	12.15	6.24	0	5.91	0	5.91	.214	1.34

The experiments summarized in Tables IB and II were carried out in a similar fashion except that sufficient of the anhydrous acids were dissolved in the absolute alcohols to make the initial concentrations of the acids approximately 7 N. The initial normalities of the acids were checked both by weighing and by titration. (Anhydrous formic acid could not be evaluated by titration in alcoholic solution, because esterification takes place too rapidly. In this case the weighed samples of acid were titrated after dilution with water.) The final concentrations of formic acid could not be determined with a high degree of accuracy even at 0° because of the relative rapidity of the hydrolysis of ethyl and methyl formates. The first experiments carried out with formic acid were discarded because of this difficulty. However, the results obtained in these preliminary experiments checked approximately those obtained in the more carefully controlled experiments here reported.

The time of heating necessary to produce approximate equilibrium varied from about one day (twenty-four hours) when formic acid was concerned, to eight or ten days when propionic acid was used.

In order to test whether ether might be formed when a fatty acid is heated continuously with alcohol, a mixture of **30** cc. of glacial acetic acid and 120 cc. of absolute alcohol was heated to 100° for 144 hours in a sealed tube. At the end of this time the mixture was fractionated using a three foot column, and no trace of liquid came over below 70°, indicating that no ether was formed.

Euler[2] previously made determinations of the hydrolysis equilibrium constants of fatty acids in accordance with the results given in Table III. He started in each case with a solution 2 N in both acid and alcohol, but in addition the solution **was** 0.25 N in hydrochloric acid. Our principal objection to his work is the fact that the hydrochloric acid which was introduced as a catalyst was present at the start in a concentration one-eighth as great as the concentration of the acid investigated. This introduced an error due to the formation of the ester of the hydrochloric acid as well as the formation of the ether mentioned above.

TABLE III

HYDROLYSIS EQUILIBRIUM CONSTANTS (EULER)

	Methyl alcohol	Ethyl alcohol
Formic acid	0.20	0.36
Acetic acid	.15	.27
Propionic acid	.15	.27

A study and comparison of the values obtained emphasizes the fact that they are not "constants" since they vary with the conditions. In the case of the weakest acid (propionic) the variations in the value are the least, but the discrepancies in the case of the strongest acid (formic) are very great. The results show that under all the comparable conditions studied the esters of formic acid are most completely hydrolyzed, the esters of acetic acid are next and the esters of propionic acid are least hydrolyzed. This order is the same as that of the strengths of the acids concerned. It is also noteworthy that the hydrolysis equilibrium constants of the esters as well as the ionization constants of the acids are nearly the same in the case of acetic and propionic acids, but in the case of formic acid both values are much higher.

Esters of Hydroxy Acids.—Hydroxy acids are materially stronger than the corresponding fatty acids as indicated by the values given in Table IV. In this table are also given the results obtained for the ethyl esters of glycolic and lactic acids and (for comparison) the values for the corresponding esters of acetic and propionic acids.

TABLE IV

ETHYL ESTERS OF GLYCOLIC AND LACTIC ACIDS

	Acid		Alcohol		Water		Ester			
	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	Initial concn.	Final concn.	K_E	$K_A \times 10^{-5}$
Acetic	..	..	..	..	..	..		..	0.296	1.8
Glycolic	5.46	2.52	9.75	6.81	10.3	13.24	0	2.99	(.44)	15.2
Propionic	..	..	..	..	..	..		..	.289	1.34
Lactic	6.45	3.80	6.45	3.80	11.7	14.35	0	2.65	(.38)	14.0

These values for the esters of the hydroxy acids, because of some "lactide" formation, do not represent true esterification equilibrium values. In spite of this fact the results are not meaningless, since the values obtained indicate hydrolysis equilibrium constants for the esters of the hydroxy acids higher than for-the esters of the corresponding fatty acids, and any correction which might be introduced to correct for lactide formation would increase rather than decrease the constants.

Although the results here presented are not wry extensive, when considered in relation to other available information which is of a qualitative nature, they are sufficient to convince us that one of the most important factors which govern the stability (in the thermodynamic sense) of esters toward water, and probably other reagents, is the so-called "negative" character of the acid group. In terms of electronic structures it seems likely that a group which is capable of exerting a pull on electrons distorts the electron shells of nearby atoms and causes the compound to be less stable. A more "negative" group should then be capable of causing more distortion and consequently more instability. The situation is quite complex, however, and it does not seem possible at present to picture with any certainty the nature of the distortion, if it exists, or to know which particular atomic shell is distorted in such a way as to cause instability.

That the "negative" character of the acid group is not the only factor which governs instability is shown by the fact that when esters with quite different structures are compared there may be no relationship between the hydrolysis equilibrium constants of the esters and the ionization constants of the acids.

Summary

An attempt was made to determine by a direct method the hydrolysis equilibrium constants of several esters to see if these constants have any relation to the ionization constants of the corresponding acids. The results seem to bear out the generalization that when esters of not too dissimilar structure are compared, the esters of stronger acids are more completely hydrolyzed under like conditions than are the esters of weaker acids. The hydrolysis equilibrium constants were directly determinable in only a very limited number of cases and were found to vary with the conditions.

EUGENE, OREGON

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

DECOMPOSITION OF DIACETONE ALCOHOL BY SODIUM HYDROXIDE IN WATER MIXTURES OF ORGANIC SOLVENTS

BY GÖSTA ÅKERLÖF

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Introduction

This paper gives a preliminary orientation toward a study of the decomposition velocity of diacetone alcohol in non-aqueous solutions. The measurements have been carried out with varying water mixtures of a number of different aliphatic alcohols as solvents. Some other solvents were used but they were either very difficult to purify or the solubility of the alkali hydroxides in their pure state was very small. Therefore the measurements with water mixtures of these solvents do not have any greater interest and will not be given here. As catalyst 0.1 N sodium hydroxide was added. The complete lack of any data regarding the thermodynamical properties of the catalyst in these solutions makes it very difficult to give a reasonably safe interpretation of the results obtained.

Experimental Methods and Materials

The method[1] used to measure the reaction velocity was the same as previously described. Errors due to evaporation of the solvent are discussed in the preceding paper[2] on measurements with weaker bases. All the different solvents used, except methyl and ethyl alcohol and glycerine, were obtained from the Eastman Kodak Co. Ethyl alcohol was refluxed and redistilled twice over burnt lime. All the others were delivered as solvents practically free from water. For a first orientation in this field further drying and fractional redistillation were regarded as entirely unnecessary. Methyl alcohol was dried over burnt lime and redistilled but no difference was found for the reaction velocity in solutions prepared with the dried or undried alcohol.

Experimental Results

A summary of the measurements is given in Table I. Their graphical representation is shown in Fig. 1. The amount of organic solvent used is always given in weight percentage (w. p.). The solutions for a weight percentage of 99 were obtained through the dilution of a weighed amount of a very concentrated aqueous solution of sodium hydroxide with the pure solvent. An allowance of 0.5% is made for water in the pure solvent. In the last column of Table I are given some measurements with mixtures of methyl and n-propyl alcohol. These solutions were made up from

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[1] Åkerlöf, THIS JOURNAL, *48*, 3046 (1926); *ibid.*, *49*, 2955 (1927).

[2] Åkerlöf, *ibid.*, *50*, 733 (1928).

the pure solvents. The sodium hydroxide concentration represents the normality in 1000 g. of the solvent. The velocity constants are given with the minute as unit of time. They have about the same accuracy as the results published in preceding papers.

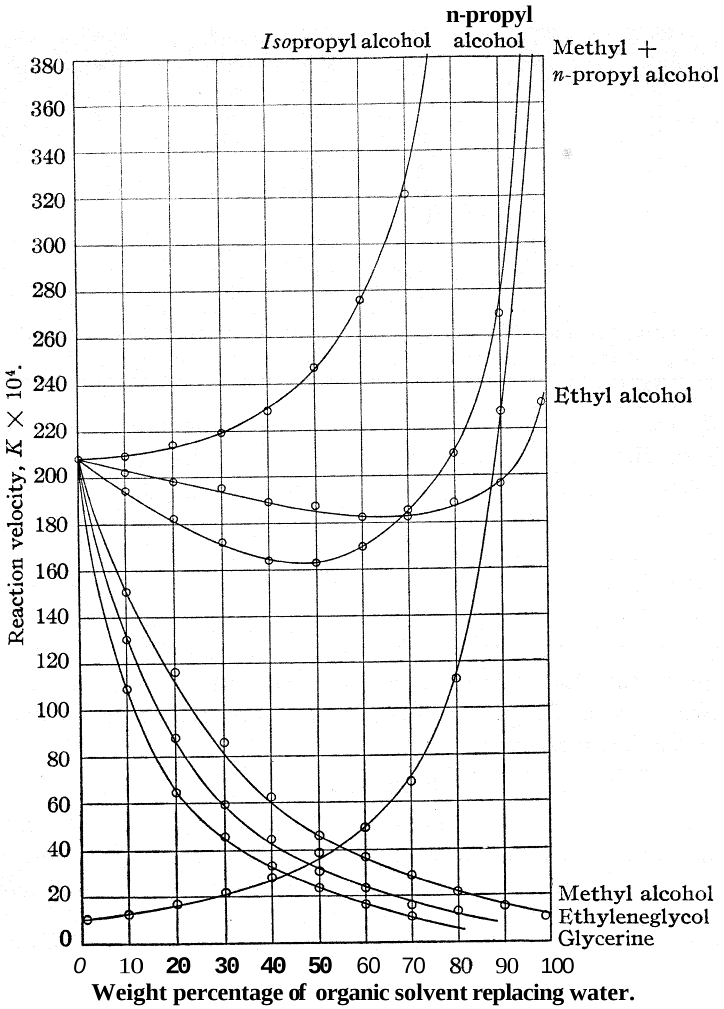

Fig. 1.—Curves for the decomposition velocity of diacetone alcohol in water-aliphatic alcohol mixtures with 0.1 *N* sodium hydroxide added as a catalyst.

The results seem to be rather remarkable. The differences in velocity for solutions in pure methyl, ethyl and n-propyl alcohol are relatively quite large. In these solutions only few hydroxyl ions might be present on account of the formation of alkali metal alcoholates. The function of

TABLE I

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL WITH 0.1 *N* SODIUM HYDROXIDE AS CATALYST IN SOLUTIONS OF WATER–ALIPHATIC ALCOHOL MIXTURES

	Values of $K \times 10^4$						
W. p.	Glycerine	Ethylene-glycol	Methyl alcohol	Ethyl alcohol	*n*-Propyl alcohol	Isopropyl alcohol	Methyl + n-propyl alcohol
0	208	208	208	208	208	208	10.3
10	109	130	151	202	194	209	12.5
20	64.4	88.0	116	198	182	214	17.2
30	45.8	59.2	86.3	195	172	219	21.9
40	32.8	44.6	62.4	189	164	228	28.0
50	23.8	30.3	46.0	187	163	247	38.7
60	16.2	21.6	38.4	182	170	276	50.8
70	10.9	15.8	28.7	182	185	321	68.4
80	...	13.2	21.6	188	209	900[a]	112
90	...	. .	15.4	196	270	..	227
99	...	. .	10.3	231	500[b]	..	500[b]

[a] Approximate value. The solution parted in two phases, one very small, around 1% of the total volume, contained more than 50% of the sodium hydroxide added.

[b] value that may have a larger error (the true value most probably higher).

the hydroxyl ion is then taken over by the alcoholate ions. With an increase in their weight and therefore also in size an increase in reaction velocity apparently follows, Thermodynamically this result was to be expected because the solubility of sodium hydroxide in the primary alcohols decreases rapidly with increasing molecular weight of the alcohol. At the saturation point the activity of the hydroxide in solution is constant and equal to the activity of the solid. At corresponding concentrations the activity coefficient of the alkali hydroxide must therefore increase with decreasing solubility. In preceding papers it was shown that the decomposition velocity of diacetone alcohol was proportional to the mean activity coefficient of the alkali hydroxide.

Conclusions

A comprehensive study of the literature regarding reactions catalyzed in non-aqueous solutions has been given by Walden.[3] Therefore in this place we will not attempt any extensive discussion of the results obtained. Only the more obvious facts will be stated.

The velocity for the decomposition of diacetone alcohol at 25° with 0.1 N sodium hydroxide as a catalyst has been measured in varying water mixtures of a number of different alcohols. The velocity in pure primary alcohols as solvents increases with increasing molecular weight of the solvent. This is the opposite of the rule found by Goldschmidt[4] and coworkers ior the formation of an ester, catalyzed by one of the halide acids

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[3] Walden, "Elektrochemie nichtwässriger Lösungen," J. A. Barth, Leipzig, 1924. The literature is covered to July, 1923.

[4] Goldschmidt and co-workers, *Z. physik.* Chem., 81, 30 (1912); 94, 233 (1920); 114, 1 (1924); 117,312 (1925); 121, 153 (1926); 124, 23 (1926).

in the same alcohols. The monomolecular reaction velocity decreased with increasing molecular weight of the solvent.

The reaction velocity in the pure alcohols decreased with increasing number of oxy groups in the alcohol. The velocity was very much higher in ethyl alcohol than in ethylene glycol solutions. The addition of dextrose with five oxy groups decreased the velocity very rapidly to values too small to be measured accurately. The velocity in solutions of isomeric alcohols is greatest for the form with the most compact alkyl group. Again Goldschmidt and co-workers found the contrary. The velocity of formation of an ester catalyzed by one of the halide acids is highest for the normal form.

The reaction velocity in solutions of some of the pure alcohols is largely influenced by the presence of small amounts of water. This influence decreases with decreasing molecular weight of the alcohol or with increasing number of oxy groups. It seems to be rather small for methyl alcohol, ethylene glycol and polyvalent alcohols. The curves for the reaction velocity in water–alcohol mixtures showed in all cases a continuous variation. Sharp bends or other peculiarities did not seem to be present.

Summary

The decomposition velocity of diacetone alcohol at 25° with 0.1 *N* sodium hydroxide as catalyst has been measured in varying water mixtures of a number of different alcohols. A short discussion of the results has been given.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, DEPARTMENT OF AGRICULTURE]

THE COMPRESSIBILITY ISOTHERMS OF HYDROGEN, NITROGEN AND A 3:1 MIXTURE OF THESE GASES AT TEMPERATURES BETWEEN 0 AND 400° AND AT PRESSURES TO 1000 ATMOSPHERES

BY EDWARD P. BARTLETT, H. L. CUPPLES AND T. H. TREMEARNE

RECEIVED DECEMBER 23, 1927 PUBLISHED MAY 5, 1928

This report is the fourth of a series from this Laboratory concerning the physical properties of hydrogen, nitrogen and their mixtures at high pressures.[1] In it are presented the results of a continuation of a study of compressibility phenomena of hydrogen and nitrogen through the temperature range from 0 to 400°.

Method.—A quantity of gas at known pressure and temperature is confined in a heavy steel pipet of known capacity. This gas is allowed to expand into a gas buret maintained at constant temperature and the

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[1] (a) Bartlett, THIS JOURNAL, 49, 65 (1927); (b) 49, 687 (1927); (c) 49, 1955 (1927).

quantity of gas determined by measurement of a fixed volume at a measured pressure not far above or below atmospheric pressure.

Preparation and Purification of the Gases.—As in the earlier work, hydrogen is prepared by the electrolysis of a solution of potassium hydroxide, and nitrogen is obtained from the fractional distillation of liquid air. The argon content of the nitrogen is believed by the manufacturers not to exceed 0.05%.[2] The 3:1 hydrogen–nitrogen mixture is prepared by "cracking" anhydrous ammonia on an ammonia catalyst at 700° and removing uncracked ammonia by means of a water scrubber. A suitable purification train described in a previous report provides for the removal of water vapor and traces of oxygen.

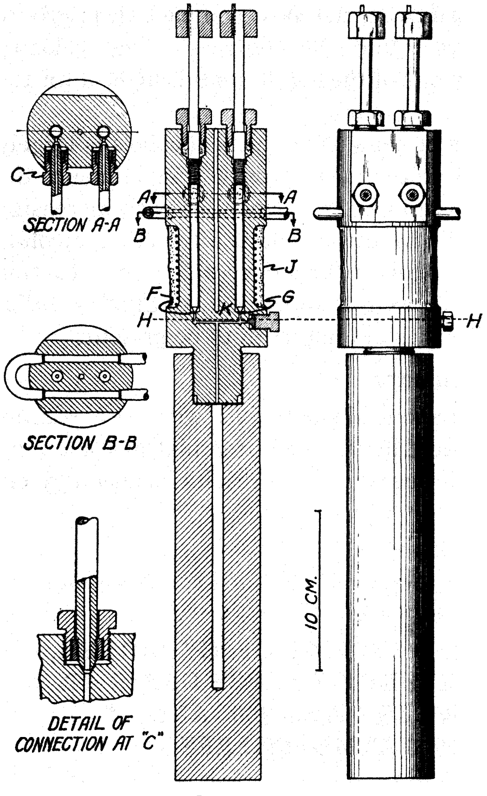

Fig. 1.—High temperature pipet.

Apparatus.— Only such changes have been made in the apparatus already described[1b] as are required to meet the changed temperature conditions. The temperature of the pipet is maintained by means of a stirred and thermostatically controlled bath of brine, water, light oil, heavy oil or molten eutectic lead–tin mixture, depending upon the temperature. At 300 and 400° manual regulation of temperature has been found to be more satisfactory.

Pipets such as were described in a previous paper are satisfactory at the temperatures below 200°. They are of chrome vanadium steel containing 1.3% Cr, 0.2% V and 0.2–0.3% carbon. At the temperatures above 200° cooling of the valve stem threads is essential and the valve stems themselves must be of a material which retains its hardness. A 13% chromium steel fulfils well this requirement. After a number of stages in development a pipet has been designed which not only is satisfactory for work at 400° but seems best suited also for work at any lower temperature.

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[2] The actual argon content of nitrogen made by rectification of liquid air is now being investigated by this Laboratory.

The compressed gas enters the pipet (Fig. 1) at F and is released at G. There is no possible error from gas trapped in valve stem packings. Valve leakage is quickly detected by means of a bubbler in the expansion line. The pipet is immersed in the bath to the depth HH. The valve stems are water cooled at BB. By means of the electrical heating unit J, heat is applied until a thermocouple at K registers the bath temperature. It is assumed that this precaution assures a uniform temperature throughout the entire body of the trapped gas.

Calibration.—All apparatus on which the accuracy of data depends has been carefully calibrated. Special mention will be made of the methods employed in calibrating the steel pipets and the dead-weight pressure gages.

The Laboratory is provided with a steel pipet of 27.38 cc. capacity which has been calibrated with mercury, both by this Laboratory and the Bureau of Standards. This pipet and the pipet to be calibrated are connected in parallel to the apparatus and filled with gas of the same composition at identical pressure and temperature (usually 100 atmospheres and 0°). After the small correction for change in capacity with change in pressure has been applied, the ratio of the pipet sizes is the ratio of the expanded volumes of gas from the two pipets. After establishing the compressibility of hydrogen this calibration, which is frequently made, is expedited by measuring the volume of expanded hydrogen from the pipet filled at some known pressure P and temperature T (usually 400 atmospheres at 0°). The capacity of the pipet is then calculated from the expression

$$V_{T,P} = \frac{V'}{P_T} \cdot \left(\frac{PV}{P_0V'}\right)_{H_2T,P} \tag{1}$$

where V is the capacity of the pipet and V' the volume of expanded gas at 1 atmosphere pressure P_0, both at constant temperature T.

The change in capacity of the pipet with change in pressure is given by Love's formula[3]

$$\Delta V = \frac{V_0}{E(r_2^2 - r_1^2)} [3(1 - 2\mu)(P_1r_1^2 - P_2r_2^2) + 2(1 + \mu)(P_1 - P_2)r_2^2] \tag{2}$$

where V is the capacity of the cylinder, E is the modulus of elasticity of steel (20.4×10^5 atmos./cm.^{2}), r_2 and r_1 are the external and internal radii of the cylinder, P_1 and P_2 are the external and internal pressures and μ is Poisson's ratio (0.287).[4]

The temperature coefficient of capacity change was derived from an equation furnished by Keyes, Joubert and Smith.[5] The numerical values of the constants are based on data of the Reichsanstalt.

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[3] Love, "Mathematical Theory of Elasticity," Cambridge University Press, **1920, p. 141.**

[4] Holborn, Scheel and Henning, "Warmetabellen," Friedrich Vieweg and Son, Braunschweig, **1919,** p. 53.

[5] Keyes, Joubert and Smith, J. *Math. Phys., Mass. Inst. Tech.,* 1, 191 (1922).

$$V_t^{Fe} = V_0(1 + 3.25 \times 10^{-5}\, t + 2.85 \times 10^{-8}t^2 - 1.65 \times 10^{-11}t^3) \qquad (3)$$

where V_0 is the original capacity, V_t the final capacity and t the change in temperature.

Pressures are established by two gages of the dead-weight movable piston type. One of the gages has been constructed with a view to both simplicity and accuracy. The weights are supported by a scale pan hung from a saddle which transmits the load to the load bearing at the top of the oscillated piston (Fig. **2A).** There are no levers. The piston diameter is 1.5875 cm. and the cylinder diameter 1.5883 cm. The effective diameter is taken as 1.5879 cm., and each atmosphere is represented by 2.0463 kg. on the piston. It has been shown by Michels[6] that while the effective area may vary because of forces other than purely hydrostatic forces, such as the distortion of the piston under pressure, the effect is negligible at pressures below 250 atmospheres. Keyes and Dewey[7] have made similar tests and have found a deviation of one part in 11,000 at 587 atmospheres, while Bridgman[8] calculated a deviation of 1 part in 500 at 10,000 atmospheres. Until further data are available it will be assumed that the error introduced from this source is much less than 0.1% even at 1000 atmospheres' pressure. The new gage has been used successfully to 200 atmospheres' pressure. The limiting factor in its accuracy is its sensitivity. This is less than 0.05 atmosphere at all pressures.

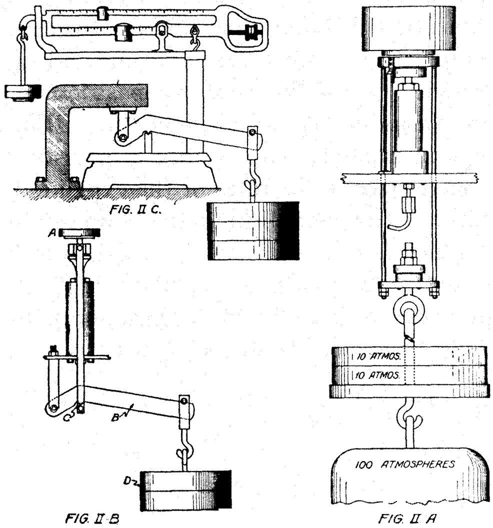

Fig. 2.—High pressure gages.

The second gage, but first in order of construction, has been a standard of reference in this Laboratory for a number of years. The effective diameter of the piston as determined by direct measurement was found to be 0.24465 cm. and the effective diameter by comparison with the newer gage 0.24457 cm. One atmosphere is represented by 194.179 g. on the piston. For pressures to 100 atmospheres weights are placed directly on the piston (Fig. 2B). Higher pressures are obtained by means of a second class lever (B) with a multiplying power of approximately 5, and a series

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[6] Michels, *Proc. Acad. Sci. Amsterdam,* *26,* *805* (1923); *Ann. Physik,* 72, *285* (1923); *Proc. Acad. Sci. Amsterdam,* 27,930 (1924); *Ann. Physik,* 73, 677 (1924).

[7] Keyes and Dewey, *J. Optical Soc. Am.,* 14,491 (1927).

[8] Bridgman, *Proc. Am. Acad.,* **47,** 321 (1911).

of weights (D) each of which is equivalent to approximately 100 atmospheres' load at the load bearing (C). The effective piston load of the lever and weights has been determined in conjunction with the Bureau of Standards. The arrangement of the equipment for the calibration is shown in Fig. 2C.

> "A previously calibrated counter scale was employed to measure the reactions at the load pivot of the lever, the procedure being as follows. The load bearing was placed on the platform of the scale, the fulcrum bearing rigidly anchored in level alignment with the load bearing and the scale balanced by means of the sliding counterpoise. The lever was then set in place and the resultant reaction on the load bearing measured by the use of calibrated weights on the fixed counterpoise. Similarly, the reactions caused by addition of the hanger, the hanger weight and the several weights were determined. After observing and recording the reactions at successive increments of load up to capacity (158.54 Kg) the loading was reduced by identical stages and the reactions at each decrement recorded."[9]

By this method each step in the loading was checked four times. The maximum deviation from the mean of several calibrations was 0.25% and the average deviation 0.07%.

Sources of Error and Limits of Accuracy of Results.—A critical survey of the method employed in collecting data for this report reveals two groups of possible errors: *(a)* the usual errors of measurement of temperature, volume and pressure; and (b) errors introduced through insufficient knowledge of the physical and chemical properties of the materials used in the investigation.

Errors in the first group should not exceed 0.1% if careful attention is given to calibration of measuring devices. However, it has been established that it is difficult to attain 0° within a heavy steel pipet completely immersed in a carefully tamped ice–water mixture, especially if the pipet is in contact with the walls of the bath. One of the pipets used in the original apparatus[10] rested horizontally in the bath, each end tied to the metal walls of the container. During use at 0°, this bath was set in a second bath and the ends of the pipet were covered with ice and water to a depth of 5 cm. In spite of these precautions there is evidence that heat was conducted through the walls of the container to the pipet. The compressibility isotherms of pure nitrogen and pure hydrogen and a 3:1 mixture of these gases have been redetermined using a stirred brine bath at 0°. Results for nitrogen are lower by an average of 0.22% and for hydrogen 0.31% than those recorded in an earlier report.[1c] The values for the 3:1 mixture differ by a maximum of 0.23% and a mean of 0.08%. This difference in the case of hydrogen and nitrogen can be ascribed to 0.6–0.8° difference in temperature. As it is not likely that so large a temperature difference existed, part of the difference may also

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[9] From the official report of the Bureau of Standards.

[10] Ref. 1 b, Fig. 1.

have been due to properties inherent in the pipets which were of the same general type of metal but of different shape and cross section. The closer agreement in the case of the mixture may be due to the fact that the published values were the average results of a number of independent runs extending over a period of nearly two years.

The second group of error sources contains the more subtle factors such as (a) stress-strain relationship and volume change, (b) viscous and plastic flow and permanent set in steels, (c) temperature and volume change relationships, (d) chemical action of the gases on the pipet material, *(e)* solubility of the gases in the pipet material and *(f)* diffusion of the gases through the walls of the pipet. In view of the fact that this is but one of a series of investigations in this field, careful presentation of the complications resulting from the above disturbing factors seems justified.

(a) Love's formula, which has been used to calculate change in volume with change in pressure, was derived for cylinders, long in comparison to diameter. It neglects end effects. The cylinders used in this investigation have heavy walls which are subjected to stresses and strains of unknown magnitude due to the tension and compression effects of the plug at one end, as well as to internal stresses and strains due to the rolling of the metal and forging of the steels. However, as the calculated maximum change in volume with change in pressure is 0.13% even at 1000 atmospheres, the uncertainty introduced at temperatures to 300° should not exceed 0.05% in the final compressibility factors. Up to 300° the coefficient of elasticity of chrome vanadium steel remains constant to within 15%.[11] Between 300 and 400° the modulus falls rapidly, possibly as much as 40%. At 400' therefore a small additional error may be introduced.

(b) The phenomena of plastic and viscous flow and strain hardening assume importance only at the highest temperature (400°) used in this investigation. Alloys of the type used in the pipets have not been studied in relation to these phenomena. However, French[12] has found the elongation of 0.24% carbon steel at 430° to be 2.5% over a period of 300 hours under a constant load of 25,000 lb. per square inch, while 13% Cr stain resisting steel showed but a few tenths of a per cent. elongation under similar conditions. It appears that no appreciable error can be introduced by neglecting the small changes caused by these factors during the few minutes in which the stress in the pipet reaches 15,000–20,000 lb. per square inch. This conclusion is substantiated by the results of calibration of the pipet before and after use at high pressure and temperature. No difference in size of the pipet has been observed.

(c) The accuracy of the temperature capacity correction for the pipet depends entirely upon the accuracy of the equation in expressing the relation of temperature and capacity at temperatures to 400°. The temperature correction at 400° is 1.65. An error of 6% in the correction would be required to introduce an error of 0.1% in results.

(d) Errors introduced through apparent change in capacity of the pipet through formation and subsequent decomposition of nitrides and hydrides in the walls of the pipet are apparently negligible. While the literature contains many references to

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[11] French, *Bureau of Standards Technologic Paper No. 205, 1921;* also private communication from J. S. Vanick, formerly of the Bureau of Standards.

[12] French, "Methods of Test in Relation to Flow in Steels at Various Temperatures," Preprint, 1926, American Society for Testing Materials.

nitride formation when iron and pure nitrogen are brought together at temperatures above 600°,[13] Noyes and Smith[14] have shown that at 460° the dissociation pressure of iron nitride (formed by action of NH_3 on iron) is greater than 20,000 atmospheres The nitrides of chromium and vanadium, if formed at all, at 400°, would be stable compounds without appreciable effect on the capacity of the pipet. Baur and Voerman[15] give the dissociation pressure of chromium nitride as about 100 mm. at 800°. Slade and Higson[16] report the dissociation pressure of vanadium nitride to be "not greater than 0.2 mm." at 1203°. There seem to he no stable hydrides of iron or the alloying metals. It is well known, however, that hydrogen forms hydrocarbons with the carbon in the steel at 475°, and this reaction may occur at lower temperatures. It is probable that the hydrogen within the pipet at high temperatures contains traces of hydrocarbons. The time of contact is short, and the effect on the compressibility measurements is believed to be negligible.

(e) (f) The phenomena of gas solubility in metals and the rate of diffusion are so closely allied in their practical effects that they will be considered together. Nitrogen is generally present in steel. Data available, all at pressures below 200 atmospheres, indicate that nitrogen is "absorbed" by iron at elevated temperatures.[13] The amount absorbed is reported to be from 0.004%[17] found in a reduced iron sponge after eighteen hours' treatment at atmospheric pressure and 450°, to 0.3% found by Andrews[18] in massive iron cooled from the molten condition after long treatment with nitrogen at 200 atmospheres' pressure. The gas absorbed at 450" seems to have been entirely reclaimed by the use of a vacuum pump and was probably "adsorbed" on the very large exposed surface, a surface roughly calculated to be 2.5×10^5 sq. cm. to a gram of iron. At the higher temperatures the presence of nitrogen may be explained by solid solution, chemical combination with the alloying metals or the presence of hydrogen from some decomposable compound of hydrogen and subsequent catalytic formation of ammonia. Doubtless there are adsorption effects on the walls of the pipet. The exposed area, however, is of such magnitude (about 30 cm.^{2}) that even should the adsorption be proportional to pressure at 1000 atmospheres, the amount of gas involved would be less than 0.005 cc. (S. T. P.) at 450°. At the lower temperatures the amount would be larger but should introduce no appreciable error even at 0°. Ryder[19] could detect no diffusion of nitrogen through steel at temperatures below 500". Even at 1200' the diffusion rate is very slow. No appreciable error in the results of the present investigation should therefore arise from solubility and diffusion phenomena in the case of nitrogen.

Facts concerning the solubility and rate of diffusion of hydrogen through iron and steel are somewhat better established. It is well known that hydrogen released at an iron cathode of an electrolytic cell quickly penetrates to a considerable depth in the electrode, even at room temperature.[20] Diffusion of this nature is apparently due to the presence of atomic hydrogen. Similar diffusion effects due to thermal dissociation of

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[13] Sawyer, *Trans. Am. Soc. Steel Treating*, 8,291 (1925), a review with 60 references; Guillet, *Compt. rend.*, 182, 903 (1926).

[14] Noyes and Smith, THIS JOURNAL, 43,475 (1921).

[15] Baur and Voerman Z. *physik. Chem.*, 52,473 (1905).

[16] Slade and Higson, *J. Chem. Soc.*, 115,215 (1919).

[17] From an unpublished report of the Fixed Nitrogen Research Laboratory.

[18] Andrews, *Engineering*, 94,860 (1912).

[19] Ryder, *Elec. J.*, 17, 161 (1920).

[20] Schmidt and Lucke, Z. *Physik*, 8, 152 (1922); Edwards, J. *Iron Steel Inst.*, (advance proof), Sept., 1924; C. A., 18, 3348 (1924); Bodenstein, *Verhandl. deut. physik. Ges.*, 3, 40 (1922).

hydrogen in steel become appreciable at 200°[21] and fairly rapid at 500°. The solubility (c) of hydrogen in steel in g. per cc. of iron[22] is given by the expression

$$c = \alpha e^{-\beta/T} \sqrt{P} \qquad (4)$$

in which α and β are constants, T is the absolute temperature and P the pressure in atmospheres. From an extrapolation of the curve presented by Borelius based on data obtained by Sieverts, it appears that at 1 atmosphere pressure and at 300°, the solubility of hydrogen is 1.2×10^{-6} g. per cc. of iron. Assuming the above expression to hold at 1000 atmospheres the solubility of hydrogen at this high pressure is 38.6×10^{-6} g. per cc. of iron, which corresponds to a volume (S. T. P.) of 0.44 cc. The actual effect of this dissolved gas on the apparent volume of the pipet can be estimated only if the rate of diffusion be known. Charpy and Bonnerot[23] observed no diffusion of hydrogen through the walls of a tube with a thickness of 0.5 mm. under 1 atmosphere pressure at temperatures below 325°. However, results obtained by extrapolating Lombard's data[24] from above 400° show that at 300° the rate of diffusion through a disk of electrolytic iron 0.162 mm. thick should be at the rate of 5.6 cc. (S. T. P.) per cm.^{2} per hour, at 1 atmosphere pressure. Lombard also found that at pressures to 1.5 atmospheres the rate of diffusion is proportional to the square root of the pressure and inversely proportional to the thickness of the metal.[25] Assuming the pressure–diffusion relationship to hold at 1000 atmospheres, there might have passed through the 0.162 mm. inner layer of the pipet chamber 88 cc. of hydrogen per minute. The pipet wall is 25.4 mm. thick. Assuming the wall thickness diffusion relationship to hold and taking into account the cylindrical form of the pipet, about 2.5 cc. of gas may escape from the outer wall per minute.

A laboratory experiment intended to determine the loss of gas by diffusion has been carried out. The pipet was filled at 1000 atmospheres' pressure at 300° and allowed to stand for one hour. The amount of gas after expansion was 1.5% less than when expansion was made immediately after closing the valves. This loss is 0.025% per minute, which on the total volume of about 2000 cc. (S. T. P.) is 0.5 cc. The difference between calculated and observed results may easily be due to the physical differences of electrolytic iron and hot rolled and forged chrome vanadium steel.

If the above assumptions and calculations lead to results of approximately the right magnitude, it is evident that at high pressure saturation of the metal takes place rapidly and that at 300° diffusion through the wall is comparatively slow. At 400° the solubility of hydrogen is increased two-fold and the diffusion rate four-fold. In practice the pipet is generally kept under pressure for ten to fifteen minutes before the valves are closed, thus giving ample time for diffusion of the gas through the inner walls. As the gas is expanded from the pipet, doubtless part of the dissolved hydrogen returns to the pipet chamber and is measured. Such degassing must take place quickly, for at this temperature no continued evolution of gas has been observed after the two or three minutes required for the expansion. Thus, while there is a small loss of gas through diffusion during the time required for expansion, there is a gain in the apparent size of the pipet due to solution and subsequent recovery of the gas. The first effect will predominate in a comparatively thin-walled cylinder such as was used by Holborn and Otto[26] and the latter effect may predominate in a thick-walled cylinder. This may

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[21] Sieverts, *Z. physik. Chem.*, **60**, 129 (1907); Ryder, *Electric J.*, **17**, 161 (1920).

[22] Borelius, *Ann. Physik*, **83**, 121 (1927).

[23] Charpy and Bonnerot, *Compt. rend.*, **154**, 592 (1912); **156**, 394 (1913).

[24] Lombard, *ibid.*, **184**, 1557 (1927).

[25] Lombard, *ibid.*, **184**, 1327 (1927).

[26] Holborn and Otto, *Z. Physik*, **23**, 77 (1924).

account in part for the fact that Holborn's compressibility factors appear too large at temperatures above 200°, while in the present investigation there is evidence that the compressibility factors may be too small.

For example, at some high pressure, in the case of nitrogen, if volume be plotted against temperature, a curve is obtained which departs but slightly from the rectilinear, but the curvature is appreciable at all temperatures from 0 to 400° and greatest in the lower temperature ranges. In the case of hydrogen, the curvature is scarcely detectable at the temperatures below 200°. It may be that the unexpected break in the curve at 300" results from solubility and diffusion effects. For instance, 1.4 cc. (S. T. P.) less of expanded hydrogen at 100 atmospheres and 3.4 cc. less of expanded hydrogen at 300 atmospheres would have resulted in a rectilinear *V-T* relationship, while at 400° the amounts are 4.6 and 8.4 cc. These volumes of gas could be accounted for as dissolved in the first centimeter of the wall thickness.

With all known sources of inaccuracy taken into account, the limit of error in the results obtained with nitrogen to 400° should not exceed **0.3%** and it is believed that average results may be depended upon to within 0.1–0.2%. The same limits hold for hydrogen to 200°. At 300°, the error may reach 0.4–0.5%, and at 400" the results are so irregular that they are presented only as experimental data without claim for high degree of accuracy.

Experimental Results

The experimental results of this investigation are presented in Tables I, II and III. In the compressibility factor, PV/P_0V_0, PV is the pressure volume product of a given gas mass under the conditions of the experiment, while P_0V_0 is the pressure volume product of the same gas mass at 0° and 1 atmosphere pressure. It has been assumed that at pressures near to atmospheric, nitrogen, hydrogen and their mixtures conform to the laws of the ideal gas. The values given in the tables at 1 atmosphere are calculated on this basis. Where comparative data are available from other sources[27] they are included in the tables together with the name of the investigator. In some instances short interpolations or extrapolations have been necessary to bring these groups of results under comparable conditions. A comparison of the new results with those of Holborn at 50 and 100 atmospheres' pressure and temperatures to 400° shows maximum deviations for nitrogen and hydrogen of 0.30 and 0.33% and mean deviations of 0.08 and 0.18%, respectively. At pressures from 100 to 1000 atmospheres and temperatures to 200° the maximum deviations from the results of Amagat are 0.60 and 0.69% and the mean deviations 0.30 and 0.39%, respectively.

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[27] (a) Amagat, *Ann. chim. phys.*, [6] 29, 68 (1893); (b) Holborn, *Ann. Physik*, 63, 674 (1920); (c) Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 169 *D* (1924); (d) Witkowski, *Krahauer Anzeiger*, 305 (1905); (e) Smith and Taylor, THIS JOURNAL, 45, **2113** (1923); also 48, 3122 (1926); (f) Vershoyle, *Proc. Roy. Soc. (London)*, 111A, 552 (1926); (g) Holborn and Otto, *Z. Physik*, **23**, 77 (1924).

TABLE I

THE COMPRESSIBILITY FACTORS, PV/P_0V_0, FOR NITROGEN

Press., atm.	Observer	0°	50°	99.85°	198.9'	299.8°	390 3°
1		1.0000	1.1831	1.3656	1.7283	2 0978	2 4621
50	Bartlett	0.9846	1.1888	1.3888	1.7683	....	
	Holborn	.9852	1.1886	1.3846	1.7656	2.1461	. .
	Smith and Taylor	.9835	1.1863	1.3826	....	....	. .
	Vershoyle	.9840	....	....	....	....	..
	Onnes	.9846	....	....	....	....	..
100	Bartlett	.9846	1.2046	1.4114	1.8071	2.1978	2.5720
	Amagat	.9910	....	....	....	....	....
	Holborn	.9856	1.2045	1.4118	1.8065	2.1953	2.5726
	Smith and Taylor	.9830	1.1985	1.4049	1.7985	....	...
	Vershoyle	.9842	....	....	....	....	...
200	Bartlett	1.0365	1.2742	1.4958	1.9073	2.3110	2.6044
	Amagat	1.0390	....	1.4908	1.9040	....	....
	Smith and Taylor	1.0340	1.2580	1.4754	1.8830	....	...
	Vershoyle	1.0346	....	....	....	....	
300	Bartlett	1.1335	1.3711	1.5971	2.0169	2.4279	2.8160,
	Amagat	1.1360	....	1.5923	2.0120	....	
400	Bartlett	1.2557	1.4870	1.7112	2.1407	2.5498	2 9422
	Amagat	1.2570	....	1.7078	2.1300	....	
600	Bartlrtt	1.5214	1.7473	1.9650	2.3914	2.8034	3.1949
	Amagat	1.5260	....	1.9563	2.3815	....	....
800	Bartlett	1.7959	2.0155	2.2273	2.6510	3.0615	3.4559
	Amagat	1.7980	....	2.2218	2.6375	....	...
1000	Rartlett	2.0641	2.2825	2.4942	2.9165	3.3195	3.7196
	Amagat	2.0685	....	....	....	....	....

TABLE II

THE COMPRESSIBILITY FACTORS, PV/P_0V_0, FOR HYDROGEN

Press., atm.	Observer	0°	50°	99.85°	198.9"	299.1°	399 3°
1		1,0000	1.1831	1.3656	1.7283	2.0952	2.4631
60	Bartlett	1.0330	1.2182	1.4026	1.7684	....	....
	Holborn	1.0311	1.2161	1.4000	1.7620	....	...
	Vershoyle	1.0311	....	....	....	....	..
	Witkowski	1.0309	....	....	....	....	..
	Onnes	1.0294	....	....	....	....	...
100	Bartlett	1.0639	1.2521	1.4359	1.8030	2.1700	2 5141
	Amagat	1.0690	....	....	....	....	...
	Holborn	1.0640	1.2498	1.4339	1.7971	....	....
	Vershoyle	1.0637	....	....	....	....	..
200	Bartlett	1.1336	1.3272	1.5105	1.8804	2.2502	2 6054
	Amagat	1.1380	....	1.5163	1.8791	....	...
	Vershoyle	1.1313	....	....	....	....	....
300	Bartlett	1.2045	1.3986	1.5836	1.9556	2.3240	2.6800
	Amagat	1.2090	....	1.5886	1.9511	....	....

TABLE II (*Concluded*)

Press., atm.	Observer	0°	50°	99.85°	198.9°	299.1°	399.3°
400	Bartlett	1.2775	1.4720	1.6563	2.0295	2.3977	2.7625
	Amagat	1.2830	....	1.6616	2.0251	....	....
600	Bartlett	1.4226	1 6160	1,7999	2.1726	2.5394	....
	Amagat	1.4315	....	1.8068	2.1713	....	....
800	Bartlett	1.5665	1.7582	1.9415	2.3157	2.6762	....
	Amagat	1.5775	....	1.9518	2.3151	....	....
1000	Bartlett	1,7107	1.9006	2.0839	2.4568	2.8125	....
	Amagat	1.7200	....	2.0958	....	....	....

TABLE III

THE COMPRESSIBILITY FACTORS, PV/P_0V_0, FOR A 3:1 HYDROGEN–NITROGEN MIXTURE

Press., ntm.	Observer	0°	25°	50°	99.85°	198.9°	299.8°
1		1.000	1.0915	1.1831	1.3656	1.7283	2.0978
50	Bartlett	1.0269	1.1219	1.2144	1.3992	1.7676	....
	Vershoyle	1.0276	....	....	....	....	....
100	Bartlett	1.0583	1.1543	1.2495	1.4298	1.8065	2.1757
	Vershoyle	1.0570	....	....	....	....	....
200	Bartlett	1.1278	1.2200	1.3282	1.5068	1.8915	2.2659
	Vershoyle	1.1244	....	....	....	....	....
300	Bartlett	1.0264	1.2995	1.4034	1.5870	1.9741	2.3519
400	Bartlett	1.2890	1.3805	1.4862	1.6700	2.0531	2.4356
600	Bartlett	1.4587	1.5510	1.6577	1.8412	2.2283	2.6086
800	Bartlett	1.6342	1.7215	1.8277	2.0130	2.3958	2.7765
1000	Bartlett	1.8029	1.8904	1.9964	2.1865	2.5648	2.9495

Practical Application of the Data

Practical application of the results presented in Tables I to III may be illustrated as follows. (*a*) The volume occupied by a known gas mass at any pressure and temperature within the scope of the table may be calculated from the expression

$$V'_{P,T} = \frac{V_0}{P}\cdot\left(\frac{PV}{P_0V_0}\right)_{P,T} \qquad (5)$$

where $V'_{P,T}$ is the volume of compressed gas at pressure P and temperature T, V_0 the volume of the gas at atmospheric pressure and 0°, P the total pressure and $(PV/P_0V_0)_{P,T}$ the compressibility factor of the gas at P and T.

(b) The pressure exerted by a known gas mass at any volume, V', and temperature, T, is most conveniently determined by graphical method. In the expression

$$\left(\frac{PV'}{P_0V_0}\right)_T = f\,(P) \qquad (6)$$

V' is the desired volume of the compressed gas. By assuming different values for P, a series of values is obtained for $(PV'/P_0V_0)_T$. These are plotted against pressure on a pressure-compressibility factor diagram for a gas of the same composition and at temperature T. The pressure exerted by the gas is the pressure indicated at the intersection of the curves.

(c) The density of any gas at any desired pressure P, and temperature T, may be calculated from the expression

$$\rho_{P,T} = \rho_0 P \left(\frac{P_0V_0}{PV}\right)_{P,T} \tag{7}$$

where $\rho_{P,T}$ is the density of the gas at P and T, and ρ_0 is the density at 1 atmosphere pressure and 0°. Until it can be established that some one of the numerous equations of state already developed apply to these gases throughout the pressure and temperature range included in this report, or until a new equation of state is developed, rectilinear interpolation for values at temperatures and pressures not shown in the table may be employed without introduction of large errors.

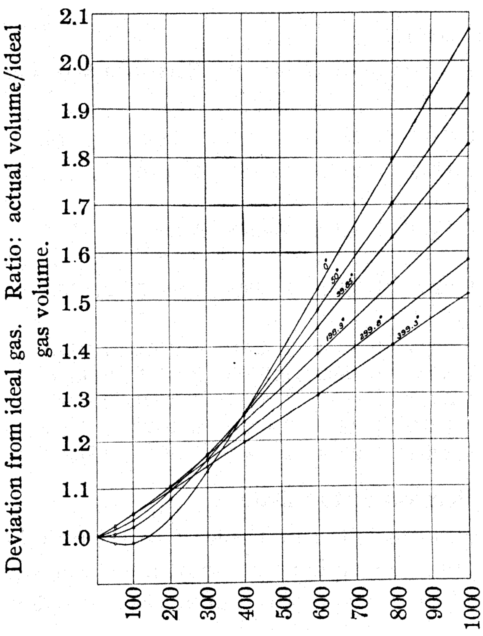

Fig. 3.—Nitrogen. Deviation from Boyle's law.

Temperature and Deviations from the Laws of the Ideal Gas.—All gases become "ideal" under the limiting conditions of zero pressure and infinite temperature. Gases under high pressure approach the "ideal" but slowly with rise in temperature. The family of curves shown in Fig. 3 pictures the deviation of nitrogen at temperatures from 0 to 400°. Pressure is plotted against the ratio $(PV/P_0V_1)_T$ in which $(P_0V_1)_T$ is the pressure volume product at 1 atmosphere and temperature T.

At pressures of 400 atmospheres and below in the case of nitrogen, the deviation ratio increases with temperature to a maximum followed by a gradual decrease. Above 400 atmospheres the deviation ratio decreases with temperature. The deviation ratio of hydrogen, on the other hand, decreases with temperature at all pressures and temperatures covered in this investigation and this deviation ratio is very nearly inversely proportional to the absolute temperature.

The Additive Rule of Volumes and Pressures.—The additive rule implies that (a) the volume occupied by a mixed gas at pressure P and temperature T is equal to the sum of the volumes of the constituents, each at pressure P and temperature T. (b) The pressure exerted by a mixed gas at volume V and temperature T is equal to the sum of the pressures of the constituents, each at volume V, and temperature T. The additive pressure rule (b), as given, is Dalton's law of partial pressure modified by Gibbs.[28] In this form it was used by Masson and Dolley[29] in their study of mixtures of argon, ethylene and oxygen.

It is well known that the values calculated on these premises rarely agree with experimental results. In the case of nitrogen and hydrogen and the 3:1 mixture of these gases in the pressure–temperature range investigated, the maximum deviation (1.66%) from the additive volume rule occurs at about 200 atmospheres' pressure and 0° (Table IV). At 200–300°, the deviation is of a magnitude scarcely greater than experimental error. No attempt has been made to calculate data for a similar complete table for the deviation from the additive pressure rule. However, in a single instance at 50°, the calculated (750 atm.) and actual (977 atm.) pressures of a 3:1 hydrogen–nitrogen mixture differ by 23.2%. The deviation is less at lower pressures. It is not difficult to explain this phenomenon if it is understood that in calculating the pressure for the one the rule ignores the so-called van der Waals "b" value of the second gas and the "a" value of the gases for each other.

TABLE IV

PERCENTAGE DEVIATIONS FROM THE RULE OF ADDITIVE VOLUMES

The volume of the 3:1 hydrogen–nitrogen mixture is greater than the sum of the volumes of the pure gases by percentages shown.

Press., atm.	0°	50°	99.85°	198.9°	299.8°
50	0.58	0.29	0.25	–0.05	..
100	1.34	.74	.47	.14	–0.06
200	1.66	1.07	.68	.23	– .07
300	1.65	0.83	.66	.16	.01
400	1.34	.70	.60	– .20	– .08
600	0.78	.54	.33	.04	.05
800	.64	.28	.19	– .15	.08
1000	.21	.03	.00	– .27	.28

It is interesting to note that a much closer agreement between calculated and observed results is obtained if the additive pressure rule be expressed, "At constant temperature the pressure exerted by one constituent in a gaseous mixture equals the product of its mole fraction and the pressure it would exert as a pure gas at a molecular concentration equal to the molecular concentration of the mixture." For instance, in the case of a 3:1 hydrogen–nitrogen mixture the following expression may be used.

$$\frac{3\left(\frac{PV}{P_0V_0}\right)_{H_2}+\left(\frac{PV}{P_0V_0}\right)_{N_2}}{4}=\left(\frac{PV}{P_0V_0}\right)_{3H_2,N_2} \qquad (8)$$

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[28] Lurie and Gillespie, THIS JOURNAL, 49,1146 (1927).

[29] Masson and Dolley, Proc. Roy. Soc. (London), 103A, 524 (1923).

V in each term represents the same molecular volume and hence the gases are present in identical molecular concentration. The deviation from this rule is less than 2% in the pressure range studied and at temperatures to 200°. The deviation seems to increase with increasing pressure and decrease with increasing temperature.

The authors take pleasure in acknowledging the friendly cooperation of the staff of the Fixed Nitrogen Research Laboratory in the solving of the many problems of this investigation. Especially are we indebted to W. E. Deming for mathematical study of the solubility of hydrogen in steel, and to W. H. Edwards and J. R. Dilley who assisted in the designing of the high pressure equipment and to the expert technicians who were instrumental in its building.

Summary

The compressibility isotherms of nitrogen, hydrogen and a 3:1 mixture of these gases have been determined through a pressure range of 1000 atmospheres and a temperature range of 400°.

The additive volume rule in the case of these gases apparently holds within the limits of experimental error at a temperature of 300°. At lower temperatures there is decided deviation.

The additive pressure rule is discussed in its various forms and is shown to hold to within 2% if defined as follows. "The pressure exerted by one constituent in a gaseous mixture equals the product of its mole fraction and the pressure it would exert as a pure gas at a molecular concentration equal to the molecular concentration of the mixture."

Some suggestions for the practical use of the experimental data are presented.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE COLLEGE]

THE EQUILIBRIUM OF NITROGEN AND HYDROGEN WITH AMMONIA IN A CORONA DISCHARGE

BY GERALD L. WENDT AND J. E. SNYDER

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The synthesis and decomposition of ammonia under the action of electric discharges were early observed.[1] Equilibrium studies were first reported by Berthelot[2] who found that 3% of ammonia by volume resulted under the action of the silent discharge. From studies of reaction rate,

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[1] (a) Deville, *Compt. rend.*, 60, 317 (1865); (b) Chabrier, *ibid.*, 75, 484 (1872); (c) Thenard, *ibid.*, 76, 983 (1873); (d) Donkin, *Proc. Roy. Soc.* (London), 21, 281 (1873); (e) de Hemptinne, *Z. physik Chem.*, 22,358 (1897).

[2] Berthelot, *Bull. soc. chim.*, [2] 26, 101 (1876).

Pohl[3] calculated that 1.2 to 1.4% of ammonia resulted at equilibrium in a Siemens ozonizer. Davies[4] found the equilibrium concentration of ammonia in a Siemens tube to be 2.88%, which varied but little with current strength and potential. According to Davies these results are in agreement with those of Falckenberg.[5] In discharges at low pressures (0.7–2.5 mm.)[6] decomposition has been found to be practically complete. Briner and Mettler[7] observed the formation of 3 to 4% of ammonia from its elements under the influence of the electric spark.

The present research shows that under the experimental conditions and at atmospheric pressure and temperature, 4.1% of ammonia by volume results from the action of the 60-cycle corona discharge between a wire and a coaxial cylinder. As a basis for comparing the action of the corona with purely thermal effects, the temperature at which this concentration of ammonia would result if the equilibrium were purely thermal was calculated and found to be 270°. A higher temperature, above 2500°, which also may correspond to the same equilibrium concentration will be discussed.

Experimental Methods

Equilibrium was approached from both sides, starting in one case with pure ammonia and in the other with a 3:1 ratio by volume of hydrogen and nitrogen. Equilibrium was regarded as established when the pressure remained constant for several hours of discharge, and when experiments with widely differing periods of discharge showed the same final gas composition.

The ammonia used in the experiments was taken from a tank containing liquid ammonia. Samples of the gas when analyzed by noting the decrease in volume from absorption in 10 cc. of 83% sulfuric acid contained in a Hempel pipet and confined over mercury, averaged 99.7% of ammonia by volume.

The discharge tube is shown in Fig. 1. It was composed entirely of Pyrex glass with the exception of the wire and the pressure regulating device. The latter consisted of mercury contained in a leveling bulb connected with the lower end of the discharge tube by rubber tubing. The high potential electrode, a platinum wire, C, 0.51 mm. in diameter (B. and S. gage No. 24), was carefully centered and sealed while under tension. The tube through which the wire was centered consisted of two sections, each surrounded by a condenser jacket. Dilute sulfuric acid was circulated through the jackets by means of an air lift. The add served as the grounded external electrode and as a cooling medium. The discharge tube was 1.2 cm. in internal diameter, 1 mm. in wall thickness and, in all, 65 cm. in length. The maximum volume including that of the enlarged end at the bottom was 70 cc.; the volume of the actual discharge space was 47 cc.

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[3] Pohl, *Ann. Physik*, 21, 879 (1906).

[4] Davies, *Z. physik. Chem.*, **64,** 657 (1908).

[5] Falckenberg, *Dissertation,* Berlin, **1906.**

[6] Hutchison and Hinshelwood, *Proc. Roy. Soc.* (*London*), **117A, 133** (1927).

[7] Briner and Mettler, *Compt. rend.*, **144,** *694* (1907). *J. chim. phys.*, **6,** 137 (1908).

Preliminary experiments showed that when starting with ammonia the final gas volume was approximately double the initial. For experiments on the decomposition of ammonia, therefore, an initial volume of about 25 cc. of ammonia (half the volume of the discharge space) was transferred to the discharge tube from an all-glass gas holder through the tube A by displacement of mercury. To avoid possible gas leakage, the pressure was maintained approximately at atmospheric during the rapid volume change resulting from the action of the corona on the ammonia. This was effected by means of the mercury leveling bulb. To prevent short-circuiting through the mercury to the lower section of the grounded electrode, the discharge was maintained only in the upper section (the acid having been removed from the lower jacket) until the volume increased sufficiently to use [illegible]

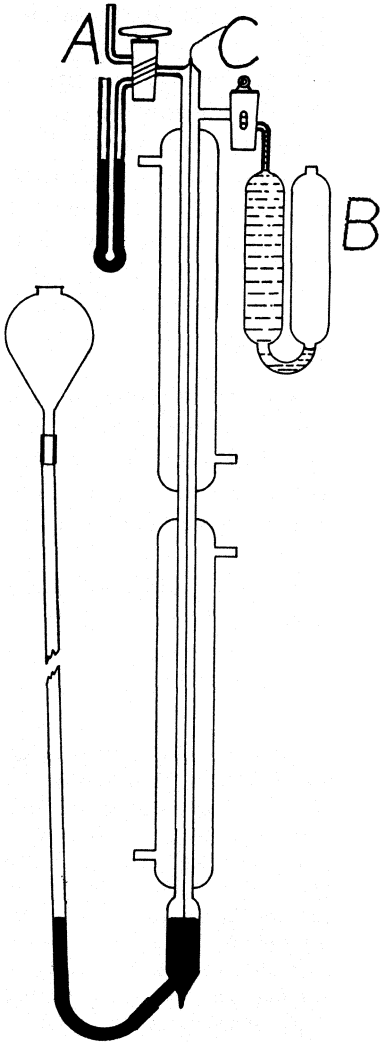

Fig. 1.

In experiments on the formation of ammonia from the elements, the nitrogen–hydrogen mixture in the ratio of exactly 1:3 by volume was prepared from ammonia in the discharge tube itself. The procedure was identical with that above, the ammonia being decomposed by the action of the discharge until the pressure remained constant. The undecomposed ammonia was then removed by absorption in concentrated sulfuric acid in the pipet B. The acid had previously been freed from air and saturated with nitrogen and hydrogen.

The electrical energy was supplied by a 60-cycle, 110-volt line. The high voltage was obtained with a 20,000-volt, 2.5 KVA., Type T-3 Thordarson transformer. The circuit included a voltmeter in the primary and a thermionic milliammeter in the secondary circuit. During the final hour of each experiment, electrical factors, temperature and pressure were carefully maintained at constant values.

The equilibrium mixture was analyzed for ammonia by absorbing a 40cc. sample in 0.01 *N* hydrochloric acid and titrating the excess acid with 0.01 N potassium hydroxide, using methyl red as the indicator.

Results

After numerous preliminary experiments and modifications in the apparatus to give the simplest conditions of operation and of measurement, consistent equilibrium results were obtained. The results of the final series of experiments are given in Table I.

TABLE I

AMMONIA EQUILIBRIUM IN A 60-CYCLE CORONA DISCHARGE

Temp., 28.5°C.; pressure, 733 mm.; sec. current, 4.2 milli-amp.; sec. voltage, 13,400 v.

Initial gas	Time of discharge, hours	NH_3 by volume, %
$N_2 + 3H_2$	15.5	4.0
	11.7	4.0
		Mean 4.0
NH_3	30.7	4.4
	21.6	4.0
	22.8	4.2
		Mean 4.2
		Equilibrium concentration 4.1

Discussion

The results show that the corona discharge yields an equilibrium mixture containing a higher concentration of ammonia than has yet been reported for any other type of electric discharge. According to the equation $3H_2 + N_2 = 2NH_3$, 71.9% of hydrogen and 24.0% of nitrogen are in equilibrium with 4.1% of ammonia. The equilibrium constant, K_p, is given by the equation

$$K_p = \frac{p_{NH_3}}{p_{H_2}^{3/2} \times p_{N_2}^{1/2}}$$

where p is the partial pressure of the respective components. Since the partial pressure is equal to the product of the concentration, c, and the total pressure, P, the equation becomes

$$K_p = \frac{c_{NH_3}}{c_{H_2}^{3/2} \times c_{N_2}^{1/2}} \times \frac{1}{P}$$

Substituting the experimental data

$$K_p = \frac{(0.041)}{(0.719)^{3/2} \times (0.24)^{1/2}} \times \frac{760}{733} = 0.142$$

To compare these results with those obtained from the analogous thermal decomposition, that is, to note the temperature to which it would be necessary to heat ammonia to effect the same degree of decomposition, requires the use of the Van't Hoff equation

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}$$

and a knowledge of the variation of the heat of reaction, ΔH, with temperature. The completed equation is[8]

$$\text{Log}_{10} K_p = \frac{2074.8}{T} - 2.494 \log_{10} T - 0.1256 \times 10^{-3} T + 0.186 \times 10^{-6} T^2 + 2.099$$

Substituting the value 0.142 for K_p and solving, T is found to be 543. The corona equilibrium for ammonia thus corresponds to a theoretical

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[8] See Larson and Dodge, THIS JOURNAL, 45, 2927 (1923).

thermal equilibrium at 543°K. or 270°C. The thermal decomposition and formation of ammonia at this temperature are so slow that it is impossible to attain equilibrium even with the use of the best catalysts.

That there is possibly a second temperature, above 2500°, at which 4.1% of ammonia would result at equilibrium is suggested by the experiments of Maxted.[9] While an increase in temperature is usually considered to result in a decrease in the ammonia concentration at equilibrium, Maxted found that above 1000" an increase in temperature results in an increase of ammonia at equilibrium. On the basis of his experimental temperature–concentration curve, a value of 4.1% for ammonia would require a temperature above 2500°. This is of interest in the interpretation of the above results since Wendt and Farnsworth[10] found that the equilibrium of carbon dioxide with carbon monoxide and oxygen in a similar corona discharge corresponds to a thermal equilibrium at 2300".

The decomposition and formation of ammonia in the corona take place, therefore, as if all the gases were heated to a temperature of 270" in the presence of an effective catalyst; or, possibly, as if all the gases were heated to a temperature above 2500". The attainment of such temperatures in the discharge tube, in which the average temperature was less than 30°, is precluded. Hence the mechanism of the corona discharge appears to be that of activating various molecular species in such a way as to increase enormously the reaction velocities, to change the ratio of decomposition and formation and to produce a shift in equilibrium corresponding to that at elevated temperatures.

Summary

The equilibrium of ammonia with a 3:1 ratio of nitrogen and hydrogen resulting from the action of a 60-cycle corona discharge between a platinum wire and a coaxial cylindrical glass electrode is such that at a pressure of 733 mm. of mercury and a temperature of 28.5°, 4.1% of ammonia by volume results under the conditions of the experiments. The temperature at which the same equilibrium concentrations would result thermally was calculated and found to be 270° and, possibly, a temperature above 2500°.

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[9] Maxted, J. *Soc. Chem. Ind.*, 37, 105T, 232T (1918); *J. Chem. Soc.*, 113, 168, 386 (1918). See also criticism by Moldenhauer, *Chem.-Ztg.*, 48, 73 (1924).

[10] Wendt and Farnsworth, THIS JOURNAL, 47, 2494 (1925).

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A THERMOCHEMICAL CONTRIBUTION TO THE STUDY OF THE SYSTEM CADMIUM-MERCURY*

BY THEODORE W. RICHARDS, HARRY L. FREVERT AND CHARLES E. TEETER, JR.

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Many investigations concerning cadmium amalgams have already been undertaken, chiefly because these substances are used in the Weston standard cell. Early workers,[1] using mainly analytical methods, thought they had discovered a number of compounds of cadmium and mercury. Later workers[2] (especially Bijl), using chiefly the analysis of cooling curves, decided that only mix-crystals, or solid solutions, exist—the system cadmium-mercury apparently belonging to the fourth type described by Roozeboom.[3] In this type of amalgam or alloy, two or more continuous series of solid solutions are formed, the residual liquid in each case being richer than the solid in the lower melting constituent. Nevertheless, from several other lines of evidence[4] it seemed possible that there might be at least one compound of cadmium and mercury. Bibliographies of the subject (up to their respective dates) are given in the paper of Richards

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* Professor Richards prepared this communication for the press, but did not see it in proof.

[1] (a) Stromeyer ($CdHg_2$), *J. F. Chem. Phys. (Schweigger)*, **22**, 362 ff. (1818); (b) Crookewitt (Cd_2Hg_5), *Jahresber. (Liebig)*, **1847-8**, p. 392; *J. prakt. Chem.*, **45**, 87 (1848); (c) Konig (Cd_5Hg_8), *J. prakt. Chem.*, **69**, 466 (1856); (d) Kerp and Bottger (Cd_2Hg_7), *Z. anorg. Chem.*, **25**, 59 (1900); H. Iggena, *Dissert.*, Gottingen, **1899**; (e) Tammann, *Z. physik. Chem.*, **3**, 445 (1889); (f) Heycock and Neville, *J. Chem. Soc.*, **61**, 888 (1892); (g) Frilley ($Hg_{12}Cd$, Hg_5Cd, Hg_7Cd_2, Hg_5Cd_2, Hg_5Cd_4, $HgCd_2$ and $HgCd_3$), *Rev. metal.*, **8**, 541 (1911); (h) Bachmetjeff, *J. Russ. Phys.-Chem. Soc.*, 26 (Phys. Abth.) I, 265 (1894); ($CdHg_4$ and Cd_4Hg_3) see note, *Z. anorg. Chem.*, **36**, 204 (1903).

[2] (a) E. de Souza, *Ber.*, **8**, 1616 (1875); V. Merz, *ibid.*, **9**, 1050 (1876); (b) Merz and Weith, *Ber.*, **14**, 1441 (1881); (c) Schumann, *Wied. Ann.*, **43**, 101 (1891); *Dissert.* (Erlangen), **1891**; (d) G. A. Hulett, *Z. physik. Chem.*, **33**, 618 (1900); (e) Mazzotto, *Estr. Atti Inst. Ven.*, 4, Ser. 7 (1892–3); abstr. in *Z. physik. Chem.*, **13**, 571 (1893); also see *Wied. Ann. Beibl.*, **18**, 312 (1899); (f) Bachmetjeff and Wsharoff, *J. Russ. Phys.-Chem. Soc.*, **25** (Phys. Abth.) I, 237–255 (1893); also *Jahresber. (Liebig)*, **1893**, *I*, 108–109; (g) Roozeboom, *Verslag Akad. Wetenschappen Amsterdam*, **4**, 1–5 (1901); abstr. in *J. Chem. Soc.*, [2] **80**, 507 (1901); (h) Bijl, *Z. physik. Chem.*, **41**, 641 (1902); (i) Puschin, *Z. anorg. Chem.*, **36**, 201 (1903); (j) Roozeboom, "Die heterogenen Gleichgewichte" (Binary Systems,) II, 1 (1904); (k) Jaenecke, *Z. physik. Chem.*, **60**, 409 (1907); (l) Bornemann and Rauschenplat, *Metallurgie*, **7**, 936 (1909); **9**, 472, 505 (1911); *J. Soc. Chem. Ind.*, **31**, 991 (1911); (m) Maey, *Z. physik. Chem.*, *50*, 200 (1905); (n) G. McPh. Smith, *Am. Chem. J.*, **36**, 135 (1906).

[3] Roozeboom (see Fig. 7, VI), *Z. physik. Chem.*, **30**, 399 (1899); G. Tammann, "Lehrbuch der heterogenen Gleichgewichte," **1924**, p. 145.

[4] (a) Kerp and Bottger's work, cf. ref. 1 d, above; (b) Richards and Forbes, *Carnegie Inst. Publ.*, No. 56, **1906**; (c) Hildebrand, Foster and Beebe, THIS JOURNAL, **42**, 545 (1920).

and Forbes,[4b] Gmelin-Kraut's "Handbuch der anorganischen Chemie,"[5] and the recent manuscript theses of two of the present authors.[6,7] Other references also are enumerated below (Refs. 8–11). Most of the references preceding 1908 are taken from the thesis of H. L. Frevert; more recent references are from the thesis of C. E. Teeter, Jr. (see references 6, 7).

In 1906, when the present research was begun, no systematic experiments had been carried out by anyone on the heats of solution of cadmium amalgams in mercury and, indeed, little has been done in this direction since. Nevertheless, such a line of work seemed likely to throw light on the nature of the amalgams; therefore it was undertaken.[12]

The apparatus at first employed was comparatively simple. Suitable quantities of mercury (1.5 to 2 kg.) were placed in a covered calorimeter of glass and the considerable falls of temperature produced by the introduction of the amalgams were measured by a good standardized mercury thermometer. The calorimeter was placed (with a surrounding air gap) in a water tight "submarine" which was immersed in a large bath. At first a correction was applied for the warming effect of the surrounding thermostat, according to Newton's law; later the determination was made adiabatically; the two methods essentially agreed. The amalgams were made with care from moderately pure metals; their compositions were inferred from the weights of the components. The inference was not entirely satisfactory since during the act of amalgamation some oxidation occurs; but it is accurate enough for the present purpose, and parallel results at any given concentration at first seemed very consistent. Typical figures are given in Table I.

After a few weeks, however, irregularities developed. These were soon attributed to differences in the mode of preparation of the amalgams and to the relative ages of the specimens. Evidently they must be due to a slow readjustment of the components of the somewhat heterogeneous mass.

The next experiments compared the heats of solution of pellets formed

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[5] Gmelin-Kraut, "Handbuch der anorganischen Chemie," Band 5, Abtheilung 2, *1189–1200 (1914).*

[6] H. L. Frevert, *Thesis* for the degree of Ph.D., Harvard University, on file at the Harvard Library, 1908.

[7] C. E. Teeter, Jr., *Thesis* for the degree of Ph.D., Harvard University, 1927, pp. *9–55.* Amalgams prepared by Teeter were used by R. F. Mehl, in the study of the Crystal Structure of the System Cadmium-Mercury. THIS JOURNAL, *50,381 (1928).*

[8] Schulze, *Z. physik. Chem.*, **105**, *177 (1923).*

[9] Smith, *Phil. Trans.*, 207,393 *(1908).*

[10] Smith, *Coll. Researches of Nat. Phys. Lab. (Teddington), 6, 137 (1910); Phil. Mag.*, [6] **19**, 250 (1910).

[11] Cohen and Moesveld, *Z. physik. Chem.*, 95, *285* (1920).

[12] H. L. Frevert carried out most of the early experimental work before 1909.

by slow, undisturbed cooling with those of finely granular samples which were stirred until solid. The negative heats of solution of the granular samples of about 25 atom per cent. composition were always at first greater than those of the slowly crystallized samples; both types showed increase with age, but the granular samples changed less, and ceased changing sooner than the large crystals. For example, certain granular specimens showed a 4% increase in 320 hours, whereas similar specimens slowly crystallized showed about a 17% increase in the same time. They tended toward the same maximum, but in the latter case it was still far off. This was to be expected if the change was due to readjustment of the concentrations of different layers of material, for stirring would tend to make finely divided crystals which would become equilibrated more quickly than large crystals.

In April, 1908, a new series of the heats of solution of the original samples, now two years old, was made. The thermochemical effects for amalgams of less than 16 and more than **33** atom per cent. of cadmium were essentially the same as before. On the other hand, aged samples between these limits, with less mercury or less cadmium, respectively, gave distinctly greater negative heat effects than before (see Table I). In other words, the amalgams which changed were those in which small amounts of liquid had filled the interstices of matted crystals. Closer investigation of contrasted samples showed the nature of the readjustment. Pellets containing 25 atom per cent. of cadmium made by fusion (apparently quite solid on the surface when cold) revealed, when freshly prepared, traces of liquid, on close scrutiny of a fresh fracture. After a few weeks or months the liquid phase disappeared entirely in amalgams containing more than **23** atom per cent. of cadmium. There was also an increase in the size of the individual crystals and an irregular change of total volume, shown by cracking of the surface of the casting. Moreover, on comparing the aged with fresh amalgams in regard to other physical properties, marked changes were noted; with age the amalgam became harder and tougher. It was evident that the solid phase gained mercury at the expense of the liquid, and therefore that at first the cadmium had been partially segregated in the first crystals.

A device for preventing this preliminary segregation of the components was the logical step to apply next. This device was used by Smith in his admirable discussion of the Weston cell[9,10] (of course unknown to us at the time). Doubtless others had applied it before. This device consists in plunging the melted homogeneous mass into a cold environment. The resulting crystallization is too rapid to allow much segregation. In the present case several amalgams (contained in thin glass test-tubes) were thus quickly solidified by being plunged when completely molten into frozen ether at −117°. Fresh samples thus prepared gave the same heats of solution as slowly cooled amalgams two years old. This is clear from the comparison of the data in Cols. 3 and 4 of Table I. The inference is obviously that the rapid quenching had accomplished in a few seconds the same extent of equilibration that had been attained in two years; or rather it had prevented original segregation, giving a product which had a degree of equilibration equal to that of the aged sample. Obviously the preceding argument is supported.

Thus there could be no reasonable doubt that the crystals first deposited on slow cooling contained more cadmium than those deposited later (as indeed was to be expected from Bijl's diagram), and that the effects of age were due to the gradual equilibration of the earlier and later deposited crystals—those earlier deposited taking mercury from those formed later and these taking mercury from the still less concentrated drops of remaining liquid. Perhaps the first clear statement of the existence of successive different layers of this kind was that made by Schumann[13] in 1891. Gore[14] had also suspected such a possibility. The phenomenon has, however, been recently denied, or at least has been declared to be so transitory as to be unimportant.[15] Cohen called it "Zonenbildung" (perhaps not a very good name, since the word "zone" has a different crystallographical meaning) and fully understood its importance." The fact of deposition of a solid solution in successive layers of different composition is at present common knowledge in metallurgical practice, where it is called "coring" or "enveloping."[16]

There follows a table of the early Harvard results just detailed, to which is added another column (the last) containing recent figures shortly to be discussed. The table explains itself, except as regards this last column.

The results before 1910 given in this table, although furnishing much light on the crystallization of these solid solutions, evidently did not completely solve the problem. The round curve at 23 atom per cent. was not easily explicable. Hence, because the available time of one of the original investigators had come to an end, the work was not published, and was held in suspense until further experimental work could be performed. This opportunity did not arise until 1924, when the third of the present authors continued it under the direction of the first.

Careful study of the early results showed a number of important points. In the first place it was evident that the method involving the solution of an apparently solid amalgam in mercury is an excellent method of determining whether or not the whole mass is really solid. Por a solid amalgam in the neighborhood of 25 atom per cent. of cadmium has a large

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[13] Schumann, *Wiedemann's Annalen*, 43, 101 (1891).

[14] Gore, *Phil. Mag.*, [5] 30, 228 (1890).

[15] Schulze, ref. 8.

[16] See, for example, C. H. Desch, "Metallography," London, 1918.

TABLE I

HEATS OF SOLUTION OF CADMIUM AMALGAMS IN MERCURY IN KILOJOULES PER GRAM ATOM OF Cd

Atom per cent. of cadmium	Fresh (Frevert, May, 1906)	Aged two years (Frevert, April, 1908)	Quenched in ether ice, (Frevert, April, 1908)	Quenched in liquid nitrogen (Teeter, 1924-26)
75.0	− 0.98	− 0.99	.....	....
66.7	....	− 2.43	.....	....
54.5	....	....	.....	− 5.7
50.0	− 6.2	− 6.1	.....	....
39.9	....	....	.....	− 9.5
33.3	−10.9	−10.8	.....	....
28.6	....	....	−12.6	....
27.3	−12.7	−13.2	.....	....
26.0	....	....	−13.7	....
25.0	−13.8	−14.3	−14.3[a]	−14.6
23.1	−13.3	−14.5	−14.4[b]	−15.4
22.2	....	....	−14.51	−15.8[c]
21.6	....	....	.....	−14.6
20.8	....	....	.....	−14.4
20.0	....	....	−13.93	−14.3
16.7	....	....	−12.11	....
5.0	....	....	− 0.001	....

[a] Mean of two determinations (14.20 and 14.45).

[b] Mean of two determinations (14.55 and 14.42).

[c] The atom per cent. in this experiment was 22.5. All the values in this last column are averages of several determinations. For example, this particular value was the mean of 4 parallel experiments, 16.4, 15.9. 15.3 and 15.6. This particular concentration gave the most trouble of all; hence the widely differing values, which were less consistent than in any other case. An explanation will be given shortly.

negative heat of solution in mercury, whereas the mercurial liquid which clings to it has almost no heat of dilution. The method, then, discriminates sharply between an amalgam which has no "mother liquor" and one containing "mother liquor." It throws, therefore, into sharp relief the effect of the "coring;" for an amalgam in which the first crystals contain an abnormal excess of cadmium must also contain minute drops of interspersed liquid, if that amalgam has the composition which would exactly and completely solidify when thoroughly equilibrated. Evidently, also, the only way to find the true "solidus point" is with a completely equilibrated specimen, since the different layers on *a* crystal cannot be analyzed separately, or in any way inferred as to their composition from the percentage proportions of the components; too much depends on the conditions of crystallization.

Further investigation involved, therefore, in the first place, the preparation of thoroughly equilibrated samples of solid amalgams. Two methods of accomplishing this suggested themselves. One of these was the crystallization of a very small proportion of solid amalgam from a large amount of liquid. The very small percentage change in the "mother liquor" due to this almost negligible deposition of solid would allow only a very small change in the composition of the layers on the deposited crystals. This scheme was therefore put into practice, and in order to separate the "mother liquor" (which would, of course, vitiate the outcome), the crystals were whirled in a powerful centrifuge kept almost at the liquidus temperature.

The device was fairly successful, but met with three difficulties: first, the tenacious clinging of liquid mercury, which could not be wholly eliminated; second, superficial oxidation of the crystals, which could be partly prevented by working wholly in an inert atmosphere in the centrifuge (a troublesome expedient) but vitiated the product; third, the difficulty of analyzing the crystals, because the exact determination of cadmium in the presence of mercury has not been quite satisfactorily solved. Hence, although on the whole these centrifuged crystals gave. nearly the same heats of solution in mercury as the quenched samples of the earlier time, the outcome is hardly worth recording here.

Much better results were obtained from the device of quenching. Already in 1908 it had been shown that cooling by frozen ether produced a nearly equilibrated sample, but no evidence was given that this sample was fully equilibrated. It seemed well worth while, therefore, to carry out a new series of experiments with yet more efficient quenching. Hence in 1925 we used boiling nitrogen (−190°) instead of frozen ether. The lower temperature is, of course, only serviceable in causing more rapid cooling; it does not affect the product after solidification. As Tammann[17] has pointed out in the case of metals, the tendency to crystallize and the velocity of crystallization increase rapidly with increased undercooling. The object was to accelerate the speed of solidification so greatly as to prevent, to maximum extent, the segregation of the components. More important than very low temperature for this end was, perhaps, the device used for plunging the liquid amalgam into the cold environment. This consisted in a so-called deflagrating spoon (such as is used in beginners' experiments on oxygen, for example) in which was placed the large globule of hot liquid amalgam. On being plunged directly into liquid nitrogen the metal thus came into immediate contact with the intensely cold liquefied gas, and the rate of cooling must have been extremely great. Solid thus prepared is less rich in cadmium than the crystals which first separate from the same liquid solution on slow cooling. It is rather, of course, that which would be attained when the whole solidified mass is completely equilibrated after years, in other words a homogeneous solid solution of the same concentration as the liquid solution from which it was made.

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[17] For example in the "States of Aggregation," Tammann (Mehl), Van Nostrand, New York, 1925, Chapter IX, p. 226 ff.

The specimens of amalgams of different compositions quenched in this effective fashion must have been more thoroughly equilibrated than any such amalgams hitherto studied. They had been made from "chemically pure" cadmium of commerce (which was doubtless pure enough for the purpose) and carefully purified mercury. The respective percentage compositions were computed from the weighed components after correction for the weights of cadmium oxidized during amalgamation, and the latter found by dissolving the oxide formed in excess of very dilute acid and titrating the excess, using a comparative method. Melting under carbon dioxide, of course, diminishes the oxidation and the possible error.

Specimens of 4 g. each of the thoroughly equilibrated amalgams thus prepared were then dissolved with careful thermochemical measurement in a large excess of mercury. in order to obtain results which could be compared with the work done nearly two decades before. Hoping to attain greater accuracy, a more complicated calorimetric method was used. This method (an isothermal one) was essentially similar to that described briefly in a paper by Farrington Daniels and one of us,[18] although somewhat improved. Since cadmium amalgams absorb heat on dissolving in mercury, the thermal change can be measured electrically by keeping the system constant in temperature. The electrical energy used was measured by means of a silver coulometer and a potentiometer. A Dewar flask immersed in a deep thermostat served as calorimeter. The heating coil was of insulated constantan wire in a close fitting silver tube bent into the form of a helix. Asphaltum paint protected the silver from the mercury in which it was immersed. The temperature change was read on a good standardized Beckmann thermometer. A loop of heavy copper wire covered with asphaltum paint served as stirrer. The amalgams, which were all crystalline solids, were dropped into the mercury by means of a hopper, a small silvered box with hinged bottom that could be tripped from the outside. The tube supporting the hopper also served for the introduction of carbon dioxide into the calorimeter. This gas was generated in absence of air and was nearly oxygen free; its presence is essential for great accuracy, otherwise oxidation during the experiment causes accidental heat. The silver coulometer was nearly immersed in a large battery jar, well stirred, and cooled by a stream of water in order to eliminate fluctuations in resistance due to heating with the passage of current. Minor variations of voltage were compensated by changing the resistance of the circuit, a less sensitive galvanometer in the potentiometer circuit being used as indicator. Current was obtained from a 6-volt storage battery which was charged continuously at a low rate.

In each measurement of heat of solution, 800 g. of mercury and 4 g. of amalgam were used. The voltage (about 0.5 volt) corresponded to 0.4 ampere through the coil. Because of the rapid solution of the amalgam, the drop in temperature was too rapid for complete compensation; hence a correction was necessary for the heat gained from the calorimeter. Readings of time and temperature were taken and a correction (5–7% of the observed heat of dilution) was applied by the Regnault-Pfaundler method. The duration of the experiment was from 5 to 8 minutes.

The possible minor sources of error were numerous but they were avoided as far as practicable by forethought and care. The variations in their net effect is shown by the comparison of parallel experiments (a footnote under Table I gives the most divergent series). The most serious was probably that due to the oxidation of cadmium; but one possible source of irregu-

[18] Richards and Daniels, THIS JOURNAL, 41, 1746 (1919).

larity not yet referred to should be mentioned. This is the fact that near the solidus point a very small change of temperature may change a completely solid mass to one containing an appreciable number of finely divided drops of liquid. Sufficient pains must always be taken to have the solid amalgam exactly at the right temperature at the moment of immersion in mercury. If the amalgam at the moment of mixing should be too cold, it would give a cooling effect slightly too large because of its heat capacity; if too warm, it would give a cooling effect distinctly too small because of its heat capacity and the presence in it of liquefied drops. Because of these difficulties, more determinations were required than would otherwise have been the case in order that the final results should have a reasonable degree of accuracy. That reasonable accuracy was attained is indicated by the fact that the results follow a consistent curve, which for amalgams above 30 atom per cent. of cadmium (where differences in quenching could not appreciably affect the result) coincides very closely with the earlier results obtained by the other apparatus. No claim for highest accuracy is made—for the present purpose consistency is more important, and of that there can be no doubt.

These results are given in the last column of Table I, and the whole of this table is plotted in the three curves in Fig. 1. Evidently the intensive quenching which the last samples had received accomplished their purpose of equilibrating the material far more efficiently than the frozen ether had done. Evidently, too, the cooling effect of the amalgam on dilution per gram atom of cadmium is greatest at the concentration 22.5 atom per cent. of cadmium, which does not correspond to any definite simple chemical composition. The single cusp in the lowest curve is obviously due simply to the complete disappearance of the liquid phase (going from left to right); and the blunting of the cusp with less perfect equilibration in the upper curves must be referred primarily to "coring," which, by segregating excessive cadmium in the interior of the crystals, prevents the existence of the full amount of solid solution at 22.5°, although some oxidation of cadmium in the early experiments may have played a minor role.

The method just described furnishes one of the best ways of determining the "solidus" point (that is, the commencement of melting) with exactness. Bijl was not able to find this point at all by means of cooling curves; he was obliged to resort to the dilatometer, which happened to serve because of the considerable volume changes involved. In otherwise similar cases in which these volume changes are small, the present method would be particularly valuable. It is satisfactory that our value of 22.5 atom per cent. of cadmium thus found for this point is very close to Bijl's value 22.9 ± found by the dilatometer (both being at 25°). Evidently any method of determining the solidus point which does not eliminate, as ours does, the inhomogeneity due to "coring" is not to be trusted—for the exact composition of the solid at the liquid–solid interface could not then be inferred exactly from the total composition even if the distribution ratio were known, because so much would depend upon the particular circumstances of the crystallization. This caution does not, of course, apply to the liquidus point (the beginning-of-freezing) because there the great mass of the solution is liquid and mobile.

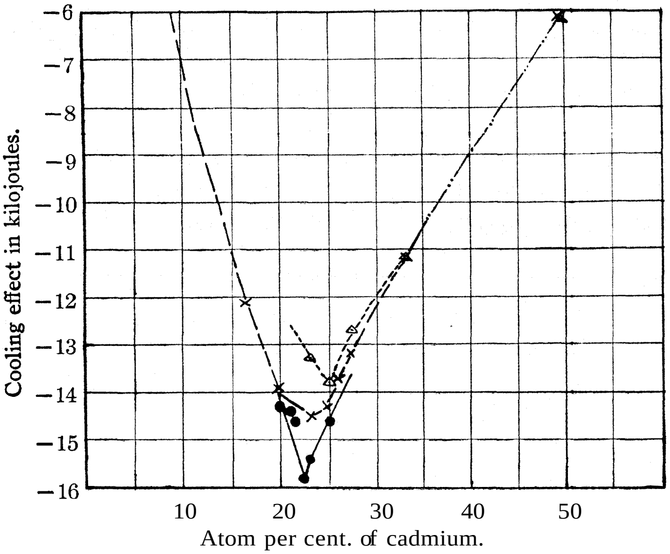

Fig. 1.—The cooling effect produced by dissolving various cadmium amalgams in great excess of mercury. Kilojoules of energy absorbed per gram atom of cadmium are plotted as ordinates; atom percentage of cadmium as abscissas. Triangles indicate 1906 experiments on non-equilibrated, slowly cooled specimens (the curve is a dotted line). Crosses show aged or quickly cooled specimens of 1908 (the curve is a broken line; where these last two coincide, the curve is broken with interpolated dots). Black circles indicate fully equilibrated specimens, quenched in liquid nitrogen, 1926.

In view of these considerations, one must define the solidus point of this kind of solid solution as the beginning-of-melting *when the solid phase is equilibrated.* Practically, it must be almost impossible to measure even by a melting curve, for the formation of the first drops will at once cause inequality of distribution of cadmium on the interface, which will take weeks or months for equilibration. Much less can it be discovered by a cooling curve, as Bijl found. But by means of successive thermochemical determinations of quenched samples it can be found exactly.

Evidently in the final curve (the lowest one in Fig. 1) there is no evidence whatever of any compound of mercury and cadmium. The cusp of the curve does not correspond to a simple definite proportion; it simply means the disappearance of liquid amalgam with increasing concentration of cadmium, as has already been said. The curve does not prove that a compound may not exist in some other part of the field, but this research has no positive evidence in that direction. The heat absorbed by dissolving a cadmium amalgam in mercury is of the order of the latent heat of melting of the solid material, although somewhat larger. This and several other aspects of the question involving different experimental methods have been studied by one of us, in part in this Laboratory, continuing the present research. These results which also, so far as they go, confirm Bijl's diagram, will be made the subject of another paper in the near future.

It is a pleasure to acknowledge our indebtedness to the Carnegie Institution of Washington, and to an anonymous benefactor of the University, for most of the apparatus employed in this research.

Summary

1. This investigation was undertaken with the aim of studying the nature of cadmium amalgams by means of thermochemical methods.

2. The large amount of heat absorbed on dissolving various cadmium amalgams in mercury was determined.

3. This heat is of the order of magnitude of the latent heat of melting of cadmium and mercury, although somewhat larger.

4. It is dependent on the weight of the solid (not including entangled drops of liquid) and on the composition of the solid.

5. Its magnitude indicates clearly whether or not the amalgam is fully solid or contains included liquid mercury, and it is therefore one of the best means of locating the exact solidus point.

6. The solidus point must be defined as the point at which liquid first appears *when the solid is fully homogeneous.*

7. An amalgam exactly homogeneous at the solidus point must, after melting and slow cooling again to that point, contain drops of liquid amalgam, because of the increased concentration of cadmium in the innermost cores of the crystals. This causes a smaller thermochemical effect on solution in mercury. The investigation thus furnishes evidence of the effect of "coring" or "enveloping." Complete equilibration takes years at room temperature.

8. The results of the investigation are consistent with the researches of Bijl and of Smith between 20 and 30°.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS OF BOSTON UNIVERSITY]

A STUDY OF MAGNETO-ELECTROLYTIC POTENTIALS

BY EDWARD O. HOLMES, JR., AND ALDEN HANDY

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Introduction

It has been found that upon allowing solutions containing dissolved electrolytes to move through constant magnetic fields, a potential difference is obtained in a direction at right angles both to the direction of flow of the liquids and the field. It is thought that the term magneto-electrolytic potential adequately describes the above effect. The existence of magneto-electrolytic potentials in solutions containing certain dissolved electrolytes was believed by Scarpa[1] to prove the presence of free electrolytic ions.

Methods of two general types have been developed for proving the presence of ions in solutions of electrolytes in the absence of an electric field, one type using gravitational and centrifugal forces and the other magnetic fields of force. Those investigators using gravitational and centrifugal means were Colley,[2] DesCoudres[3] and Tolman,[4] while others using magnetic fields were Guthrie and Boys,[5] Ostwald,[6] Franklin and Freudenberger,[7] and Scarpa.[1]

As the work presented herewith enlarges upon that of Scarpa, it would not be out of place to outline briefly the essential features of his work. Scarpa believed that if a flowing solution containing dissolved electrolyte actually contained free ions they would be forced to opposite sides of the stream in a magnetic field, thereby causing a potential difference. He was able to measure this potential difference across electrodes inserted in side tubes placed at right angles to the direction of flow of liquid and of the magnetic field. Solutions of copper and of zinc sulfate with electrodes of copper and of zinc, respectively, were used. In conclusions based upon but six readings in which he varied the flow velocity and the field strength, he derived an equation, neglecting osmotic forces, which proves to be the law of the dynamo, e.m.f. = $HVL \times 10^{-8}$, where H is the field strength in Gauss, L the length of the conductor in cm. and V the linear velocity of the wire in cm./sec. On account of the dearth of data presented and

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[1] Scarpa, *Gazz. chim. ital.*, 54,860 (1924).

[2] Colley, J. *St. Petersburg Chem. Phys. Ges.*, 7, 33 (1875); *Pogg. Ann.*, 157, 370, 624 (1876); *Wied. Bei.*, 5,451 (1881); *Wied. Ann.*, 17, 55 (1882).

[3] DesCoudres, *Wied, Ann.*, **49**,284 (1893); *ibid.*, 59,232 (1896).

[4] Tolman, *Proc. Am. Acad. Arts Sci.*, **46**, 5 (1910).

[5] Guthrie and Boys, *Phil. Mag.*, 8,449 (1879) ; 10,328 (1880).

[6] Ostwald, *Z. physik. Chem.*, 2, 270 (1888).

[7] Franklin and Freudenberger, *Phys. Rev.*, **25**,294 (1907).

the interesting features not investigated by Scarpa, the effect seemed worthy of further study.

Present Work

The relations between the potential difference measured and the concentration of the electrolyte, the flow velocity of the electrolyte, the strength of the magnetic field, the position of the cell with respect to the center of the magnetic poles and the chemical nature of the solute were investigated in turn. The change of resistance of solutions of electrolytes while flowing in a magnetic field was determined.

Experimental Part

Procedure

The solutions of electrolytes under investigation ran under the influence of gravity through a vertical tube placed between the flat centers of the conical poles of a large Weiss electromagnet. To the opposite sides of this tube were attached horizontal side arms containing copper electrodes (sealed in with de Khotinsky cement). This cell was then centrally placed in the magnetic field. In the first series of determinations in which the effect of concentration on the generated potential difference was measured, a glass cell was used but in later runs this was replaced by one made of hard rubber sheet, drilled so that a uniform and easily measurable bore could be obtained. Into the top and bottom of this rubber matrix were sealed glass entrance and exit tubes and on each side the tubes containing

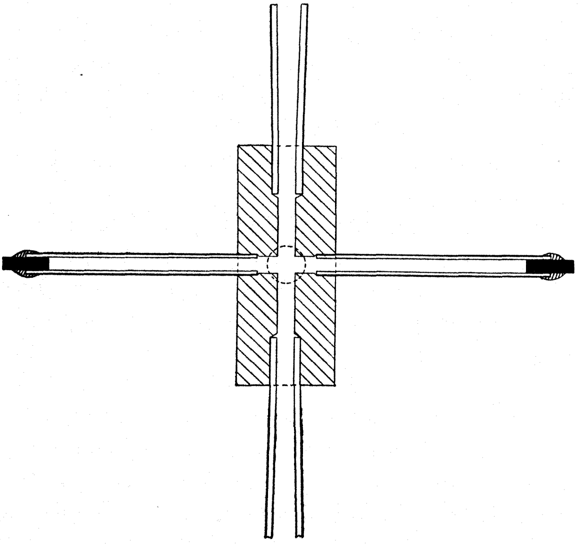

Fig. 1.

electrodes. Fig. 1 shows the construction in detail. It was necessary to place the electrodes several centimeters from the center of the vertical stream of the dissolved electrolyte so that no frictional electromotive force would be generated due to the turbulence of the flowing solution.

The rate of flow of the solution was determined by measuring with a stop watch the time for a definite quantity to pass through the cell. Knowing the diameter of the vertical hole through the cell, the linear velocity could be computed. Individual readings were taken on every run as a sufficiently reliable constant could not be obtained.

The potential difference was measured on a Wolf potentiometer connected to a sensitive d'Arsonval galvanometer. There was a residual electromotive force which could not be entirely eliminated even on long periods of short circuit. Its value had to be read before and after each run and subtracted from the maximum reading.

This residual electromotive force was usually constant but if it changed more than a few millivolts during the run the results were discarded. Scarpa[1] experienced this difficulty also. Readings for the maximum potential difference produced were always taken near the time of half flow, although on account of the large surface of the liquid in the upper container this precaution was hardly necessary. Fig. 2 shows the arrangement of the apparatus. The solutions used were analyzed for copper by electrolytic deposition, for zinc by precipitation with diammonium phosphate and for sulfate by precipitation with barium chloride.

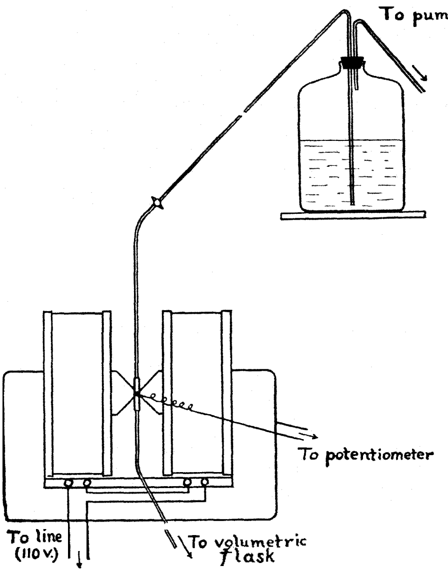

Fig. 2.

Effect of Concentration on Potential Difference

It was necessary before any other runs were made to see whether the potential difference produced was a function of the concentration of the electrolyte used, so that means might be found for keeping the concentration constant if necessary. The following results were obtained for constant field intensity corrected to constant flow.

Each of the above reported readings is a mean of several observations. It can be seen by inspection of the table that the potential difference is

TABLE I

CONCENTRATION *vs.* POTENTIAL DIFFERENCE

Molal concn., $Cu(NO_3)_2$	Vel. of soln. in liters per min.	Potential diff. in volts	Potential diff. corr. to 1.25 liters per min.
2.49	1.25	0.0045	0.0045
.259	1.25	.0043	.0043
.0326	1.23	.0042	.0043
.0033	1.15	.0041	.0044
		Mean	.0044

not a function of the concentration. Obviously this is not a concentration cell as might reasonably be expected on primary consideration.

Effect of Velocity of Solution on Potential Difference

If the solution of electrolyte affords metallic conduction, then according to the law for metallic conductors, $\text{e.m.f.} = HVL \times 10^{-8}$, the potential difference produced should be directly proportional to the linear velocity of the electrolyte and the potential difference divided by the velocity should be constant. In order to illustrate the accuracy of readings obtained, the latter are given in full in this case while subsequent data are the mean of two or more readings.

TABLE II

VELOCITY OF SOLUTION *vs.* POTENTIAL DIFFERENCE

H = 23,000 Gauss. Concn. $CuSO_4$ = 0.0967 molal. Pole separation = 1.00 cm.

Run	Linear vel. of soln., cm./sec.	Mean linear vel., cm./sec.	Pot. diff., volts	Mean pot. diff., volts	Constant obtained, (P. D./vel.) × 10^4
1	150	150	0.0128	0.0128	0.85
2	144		.0121		
	144	144	.0123	.0122	.85
3	137		.0117		
	135	136	.0120	.0118	.87
4	107	107	.0094	.0094	.88
5	94.6		.0081		
	94.4	94.5	.0081	.0081	.86
6	59.0		.0051		
	59.0	59.0	.0051	.0051	.86
7	56.7		.0046		
	56.4	56.G	.0049	.0047	.84
8	28.2		0023		
	28.2	28.2	.0024	.0024	.83
9	20.6		.0018		
	20.4	20.5	.0016	.0017	.83
10	17.5		.0015		
	17.5	17.5	.0015	.0015	.86
				Mean	.85

The above table consists of two series of runs made on different days; a fairly good constant is obtained for a nine-fold change in solution velocity.

It was impossible to prevent the magnet from heating on long runs and as the permeability of the core changes with temperature the field must necessarily have varied somewhat during the course of the runs in spite of the fact that the exciting current was kept constant.

Effect of Field Strength on Potential Difference

If this is a case of metallic conduction as suggested by Scarpa's results,[1] then the potential difference must be proportional to the field strength. The strength of the magnetic field was carefully measured by the usual method of determining the change in resistance of a calibrated bismuth spiral placed in the center of the field. Table III gives the results obtained and also includes the value for the electromotive force based on the law of the dynamo, and the difference between these values and those observed.

TABLE III

EFFECT OF FIELD STRENGTH ON POTENTIAL DIFFERENCE

Concn. $CuSO_4$ = 0.0967 molal. Bore of cell = 4.35 mm. Pole separation = 1.00 cm.

H, Gauss	P. D. corr. to 112.7 cm./sec.	$(H/P.D.) \times 10^{-5}$	E.m f. calcd.	Diff. between calcd. and obs.	Diff., %
8,300	0.0033	25.1	0.0041	0.0008	19
12,900	.0052	24.8	.0063	.0011	17
16,400	.0067	24.5	.0080	.0013	17
19,200	.0079	24.3	.0094	.0015	16
21,200	.0087	24.4	.0104	.0017	16
22,200	.0091	24.4	.0109	.0018	16
22,800	.0093	24.5	.0112	.0019	17
	Mean	24.6		Mean	17

An examination of the table will show a constant value for the field strength divided by the potential difference observed. However, it should also be noticed that there is a constant difference between the observed and the calculated values for the electromotive force (to be explained in a later section).

Relation of Position of Cell to Potential Difference

In order to ascertain whether the time required to displace the ions by a magnetic field (that is, if they actually are displaced) was measurable, the position of the cell was varied from a point directly above the center of the magnetic poles and about even with the upper edge of the pole to one an equal distance below, taking care to move the cell along a vertical axis between these two points. The strength of the field was determined over this range with the same bismuth spiral used to calibrate the field strength at constant pole separation.

The two curves obtained for copper sulfate (0.0967 molar) are plotted in Fig. 3 to the same scale but are slightly displaced to indicate more clearly any difference in form. Were this a case of metallic conduction in liquids the two curves should coincide at all points upon being superimposed. On the other hand, if the ions are responsible for the potential difference and require an appreciable time element to be magnetically displaced then the AV curve should be shifted bodily to the left with respect to the H curve. The fact that no apparent shift occurs does not necessarily prove that the ions are not displaced as this process may be very rapid and follow the value for the field strength closely. That the two curves would not coincide if superimposed cannot be adequately explained in the light of our present knowledge but might be caused by the bismuth spiral being a flat disk while the portion of the cell between the side arms is cylindrical.

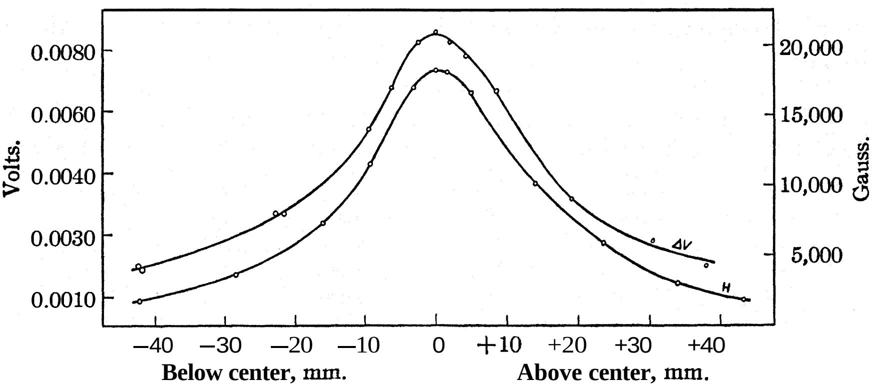

Fig. 3.

Effect of Chemical Nature of Electrolyte on Potential Difference

Up to this point all of the work with the hard rubber cell had been done with the same copper sulfate solution. The effect of the chemical nature of the solute on the potential difference generated was next studied. The results are given in Table IV.

The constants obtained in the above runs agree well with those for copper sulfate with the exception of those for potassium sulfate. In this case it is believed that they are near enough to the mean to suggest that the same phenomena are taking place as in the others.

It was believed that the constant difference between the observed and the calculated results was due to one of two causes, either the effective bore of the cell at the point where the side arms entered was greater than the value used (the side arms being of the same diameter as the central vertical tube) or the difference was due to osmotic forces set up by the displaced ions,

Consequently, a new cell was made on the same general plan as that used hitherto except that the bore of the side arms at the point of entrance into the main vertical tube was made much smaller (1.0 mm.), so as to

TABLE IV

EFFECT OF SOLUTE ON POTENTIAL DIFFERENCE

Solute	Molal concn.	*H*, Gauss	P D.. v.	Linear vel., cm./sec.	P. D., v. (at 112 7 cm./sec.)	Calcd., P. D., v.	% Diff. between calcd. and obs. P. D., %	(P. D./vel.) $\times 10^4$	$(H/P. D.) \times 10^{-5}$
$Cu(NO_3)_2$	0 107	23,200	0 0111	132	0 0095	0 0133	17	0 84	24
$Cu(NO_3)_2$	107	19,400	0096	135	0080	0114	18		24
$Cu(NO_3)_2$	107	19,400	0083	121	0077	0102	19		25
$Cu(NO_3)_2$	107	19,200	0047	69	0078	0058	19	.	25
$Cu(NO_3)_2$	.107	19,200	0044	66	0075	0055	20		26
$Cu(NO_3)_2$	107	19,200	0026	34	0086	0028	7	.	22
$Cu(NO_3)_2$	107	19,200	0023	32	0081	0027	15		24
$Cu(NO_3)_2$ =	.106	23,200	0109	134	0091	0135	18	81	25
and									
$ZnSO_4$ =	.163	19,300	0092	134	0077	0112	18	..	25
$ZnSO_4$	.1163	23,000	0110	136	.0091	0136	19	.81	25
$ZnSO_4$	.1163	19,600	0056	81	0078	0069	19	.	25
$ZnSO_4$	1163	19,300	.0097	134	0082	0114	15	..	25
	1156	23,200	0106	134	0089	0135	21	.79	26
K_2SO_4	.1156	23,200	0036	46	0086	0046	22	..	26
K_2SO_4	.1156	19,200	0092	135	0077	0113	19	..	25

affect as little as possible the effective diameter of the vertical stream of solution at this point.

The results obtained with this new cell are presented in Table V.

TABLE V

RESULTS WITH NEW CELL

Concn. $CuSO_4$ = 0 0415 molal. **Diam. vert. tube** = 4.2 **mm. Diam.** side **arm** = 1.0 **mm.**

Time in secs. for one liter	H, Gauss	P. D. obs., v.	P. D. corr. to one liter per min.
61.2	23,000	0.0113	0.0115
62.4	23,000	.0108	.0112
66.6	23,000	.0100	.0111
59.4	23,000	.0114	.0113
61.8	23,000	.0113	.0116
64.8	23,000	.0107	.0116
61.0	23,000	.0118	.0120
59.8	23,000	.0115	.0115
66.4	23,000	.0102	.0113
59.8	23,000	.0114	.0114
59.6	23,000	.0116	.0115
		Mean	.0115 (theor. **val.** = .0116)
60.4	19,600	.0099	.0100
60.4	19,600	.0100	.0101
63.4	19,600	.0096	.0101
61.2	19,600	.0099	.0098
62.0	19,600	.0096	.0099
		Mean	.0100 (theor. **val.** = .0099)

TABLE V *(Concluded)*

Time in secs. for one liter	*H*, Gauss	P. D. obs., v.	Calcd. P. D.
271.6	23,500	.0025	.0026
93.0	22,900	.0072	.0074
93.2	22,900	.0074	.0074
94.6	22,900	.0074	.0073
98.0	22,800	.0072	.0069
102.6	22,800	.0066	.0066
99.0	22,800	.0070	.0070
99.2	22,800	.0070	.0070
100.6	22,800	.0070	.0069
99.2	22,800	.0070	.0070

From an examination of the table it is evident that our results check the theoretical value calculated on the rule of the dynamo within the limit of experimental error.

Limits of Detectability of Potential Difference

Concentration.—With a solution of copper sulfate so dilute that no color was apparent to the eye even after adding ammonia but still containing enough copper to give a red tinge with potassium ferrocyanide, results were obtained of the same order of magnitude as with more concentrated solutions. However, the sensitivity of the galvanometer was decreased markedly due to the extremely high resistance of the cell, which was about seven thousand ohms when filled with a tenth molal solution.

Minimum Velocity.—With the system containing an approximately tenth normal copper sulfate solution (0.0967 *M*) a detectable potential (0.0002 volt) was obtained with a linear velocity of solution of **0.75** cm./sec.

Resistance of Flowing Electrolyte in Magnetic Field

The resistance of the solution of electrolyte was measured in a stationary state with no field and then flowing with full field strength. As a source of alternating current an electron tube sine wave oscillator was used but as the bridge coils were of a poor quality the measurements were of an accuracy of about 1%. Within this range of error no difference in resistance could be detected.

Attempts to Detect Actual Magnetic Displacement of Ions

As another method of approach a water solution of phenolphthalein was passed through a glass cell (of similar construction to that first used) placed in the center of the field in order to determine whether the phenolphthalein would be caused to dissociate and the phthalate ions thereby formed be concentrated in one side arm—which ionization, if in excess of 6%, would be evidenced by coloration. Negative results were obtained.

Following this line of reasoning a saturated solution of sodium chloride replaced the phenolphthalein solution. If the sodium ion were concentrated in one side arm and the chlorine in the other a precipitation of undissociated sodium chloride should take place, at least temporarily, due to the common ion effect. No such precipitate was observed.

The three above described experiments offer no evidence that the solute while passing through a magnetic field is caused to dissociate or that the ions are actually displaced.

Theoretical Section

Although the results seem to indicate that the solution behaves like a metallic conductor (flowing electrons) a theoretical consideration of the phenomena will show that the displacement of the ions due to their motion in a magnetic field can as well account for the results obtained, even when osmotic forces are taken into consideration.

Let us consider an imaginary cell composed of a cube of liquid (Donnan[8] on the Hall Effect in liquids). This cube is moved through a magnetic field at right angles to the lines of force; the positive ion will be moved toward one vertical face of the cube and the negative ion toward the opposite face according to the right-hand rule of the dynamo. The ions would therefore pass through the opposite faces of the cube into the spaces beyond, which can be imagined to be adjacent cubes (or the side arms in an actual cell). This causes the formation of two electric layers, each on an opposite face of the central cube. The potential gradient due to the two layers of charged particles (ions) constitutes a force tending to oppose and partially annul the magnetic force displacing the ions. Consider one face of the cube. Inasmuch as a number of ions have been moved from the central cube to an adjoining cube the osmotic force due to this type of ion in the latter is now greater than the osmotic force due to the same kind of ion in the central cube, constituting an excess of osmotic force in a direction opposing the magnetic force.

Due to the increase of one type of ion in an adjacent cube, according to mass action the equilibrium must be displaced with the formation of a larger aumber of undissociated molecules and a subsequent decrease of ions of the opposite type. In the central cube, due to a loss of ions of the first type (let us say the positive ion), there will be an equilibrium shift in the opposite direction with the formation of more negative ions and a subsequent loss of undissociated molecules. This shift in equilibrium tends to decrease slightly the osmotic force due to the positive ions, to cause an increase in the negative ions in the central cube over that in the adjacent cube and thereby produce an osmotic force tending to move negative ions from the central cube into the adjacent cube. In the same way it creates an osmotic force due to the increase in the number of undissociated molecules in the adjacent cube over the number of the same in the central

[8] Donnan, *Phil. Mag.*, **46, 465** (1898).

cube. When a stationary state is attained there must be an equilibrium among these several forces and the amount of matter transported through the face of the central cube in one direction into the adjacent cube must be exactly equal to that transported in the opposite direction.

It will be remembered that the above discussion concerns the relation between the central and one adjacent cube. The same reasoning applies to the relation between the central cube and that on the opposite side.

The phenomena discussed above may be expressed mathematically as follows. Let D = cell diameter; V = linear velocity of solution; ω = valence of ion; H = field strength in Gauss; N = Avogadro's number; a = fraction of total number of molecules ionized; C = concn. in gram moles per cc.; n = number of ions given on dissociation; ϵ = unit electrical charge; u_1 = vel. of Cu^{++} ion in cm. per sec. under unit force; u_2 = vel. of SO_4^{--} ion in cm. per sec. under unit force; u_3 = vel. of $CuSO_4$ ion in cm. per sec. under unit force; dE/dx = potential gradient due to magnetic separation of ions; z = excess concn. of $CuSO_4$ due to equilibrium shift.

In the following discussion any force acting from left to right (according to the ordinary geometrical convention) is considered as a positive force. Assume copper sulfate to form an "ideal" solution.

Let us consider the forces common to cubes 2 and 3 (see Fig. 4).

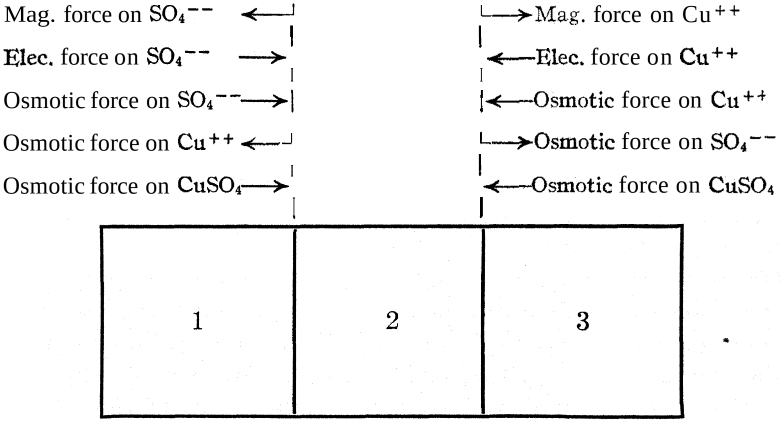

Fig. 4.

$$\text{Magnetic force on } Cu^{++} \text{ ion} = \omega\epsilon vH \qquad (1)$$

$$\text{Electric force on } Cu^{++} \text{ ion} = -we\frac{dE}{dx} \qquad (2)$$

$$\text{Osmotic force on } Cu^{++} \text{ ion} = -\frac{RT}{\alpha C_1 n}\left(\frac{d\alpha C_1 n}{dx}\right) \qquad (3)$$

$$\text{Osmotic force on } SO_4^{--} \text{ ion} = -\frac{RT}{\alpha C_2 n}\left(\frac{d\alpha C_2 n}{dx}\right) \qquad (4)$$

$$\text{Osmotic force on } CuSO_4 \text{ molecule} = \frac{RT}{(1-\alpha)C_3}\left(\frac{d(1-\alpha)C_3}{dx}\right) \qquad (5)$$

The above equations apply to conditions existing between the cubes 2 and 1 with appropriate changes in symbols. For example, the magnetic force acting upon the SO_4^{--} ion, which carries two negative charges, would cause the ion to move in a negative direction and would then be denoted as a positive force.

Imagine cubes 1 and 3 being brought into contact upon removal of cube 2 and consider the flux of matter across the common face. The two osmotic forces due to the same type of ion will be merged into one for the sake of simplicity, inasmuch as they act in the same direction.

Flux of Cu^{++} due to magnetic force $= \omega\epsilon v H u_1 n\alpha CN$ (6)

Flux of SO_4^{--} due to magnetic force $= \omega\epsilon v H u_2 n\alpha CN$ (7)

Flux of Cu^{++} due to electric force $= -\omega\epsilon \frac{dE}{dx} u_1 n\alpha CN$ (8)

Flux of SO_4^{--} due to electric force $= -\omega\epsilon \frac{dE}{dx} u_2 n\alpha CN$ (9)

Flux of Cu^{++} due to osmotic force $= -\frac{RT}{\alpha Cn}(u_1)\frac{d(n\alpha C)}{dx}$ (10)

Flux of SO_4^{--} due to osmotic force $= -\frac{KT}{\alpha Cn}(u_2)\frac{d(n\alpha C)}{dx}$ (11)

Flux of $CuSO_4$ due to osmotic force =

$$\frac{RT}{(1-\alpha)C}\ \frac{-\alpha)(C+z)]}{dx} - \frac{d[(1-\alpha)(C-z)]}{dx}\Big] \qquad (12)$$

Due to osmotic diffusion forces the Cu^{++} ion tends to diffuse through the common face of cubes 1 and 3 and at the same time the SO_4^{--} tends to diffuse in the opposite direction. Although in the case of a binary electrolyte such as copper sulfate these forces are equal and opposite, due to the differencein mobility of the ions, more of one type will pass through this face than of the other. Hence, another double layer will be established due to the excess charges on one side of this common face (similar to an electrolytic diffusion potential where both ions are diffusing in the same direction). The direction of the potential gradient of the double layer resulting from diffusion will depend upon the relative mobilities of the ions. The osmotic forces due to the undissociated copper sulfate molecules are equal and opposite, as a study of the equilibrium conditions will show.

Combining the several equations into a general equilibrium equation, the sum of the fluxes equals zero. Inasmuch as equations (10), (11) and (12) represent electrically the double layer due to diffusion forces (mentioned above) the term $K dE_1/dx$ will be substituted.

$$\omega\epsilon v H(u_1 + u_2)\alpha CN - \omega\epsilon \frac{dE}{dx}(u_1 + u_2)n\alpha CN \pm \frac{dE_1}{dx}K = 0$$

or, simplifying

$$vH = \frac{dE}{dx} \pm \frac{1}{\omega\epsilon(u_1 + u_2)n\alpha CN}\left(\frac{dE_1}{dx}\right)K = 0$$

Multiplying by D

$$DvH - D\frac{\mathrm{d}E}{\mathrm{d}x}{}^{*}\frac{D}{\omega\epsilon(u_1 + u_2)n\alpha CN}\left(\frac{\mathrm{d}E_1}{dx}\right)K = 0$$

However

$$D\frac{\mathrm{d}E}{\mathrm{d}x} = \text{e.m.f.}$$

Rearranging the above equation

$$\text{E.m.f.} = DvH \pm \frac{D}{\omega\epsilon(u_1 + u_2)n\alpha CN}\left(\frac{\mathrm{d}E_1}{\mathrm{d}x}\right)K = 0$$

This equation represents the rule of the dynamo plus or minus the last term, which must be extremely small owing to the fact that Avogadro's constant (N = 6 X 10^{23}) appears in the denominator, which more than offsets the value of ϵ in coulombs.

On account of the minuteness of this last term, the effect can be used as the basis of a method for the continuous recording of flow velocities.

Summary

In solutions of electrolytes flowing through magnetic fields a potential difference is developed at right angles to the direction of flow and that of the field, for which the term magneto-electrolytic potential is suggested.

This potential difference is independent of the concentration and nature of the dissolved electrolyte but is proportional to its linear velocity and the field strength.

Although the above appears to be a case of metallic conduction in solutions of electrolytes and to obey the rule of the dynamo it may equally well be explained by assuming the ions to be displaced. An equation may be derived which is essentially the rule of the dynamo with an added term accounting for the osmotic forces, which is extremely small.

No conclusive evidence of the actual displacement of an ion could be found. No difference in conductivity of a solution flowing through a magnetic field from that of the same solution in a stationary state out of the field was found, showing that ions are not created by magnetic dissociation of the molecules.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE HEAT OF FORMATION OF MOLECULAR HYDROGEN[1]

BY F. RUSSELL BICHOWSKY AND L. COVELL COPELAND

RECEIVED FEBRUARY 13, 1928 PUBLISHED MAY 5, 1928

The heat of association of atomic hydrogen has been measured by several indirect methods, the values obtained ranging from 00,000–107,000 calories. In this work a new determination has been made by a direct calorimetric method. The basic principle of this method can best be explained by reference to Fig. 1. Hydrogen is admitted to the discharge tube D at a known rate of flow by the capillary A. The partially dissociated gas passes through a small hole in B and is catalytically associated on the platinum calorimeter C. The temperature rise of the calorimeter gives the energy change of association. The percentage of atomic hydrogen causing the change is determined by the difference in the pressure of the gas before passing through the small hole under steady state conditions of no dissociation (that is, with no discharge) and the pressure of the steady state conditions of dissociation (that is, with discharge).

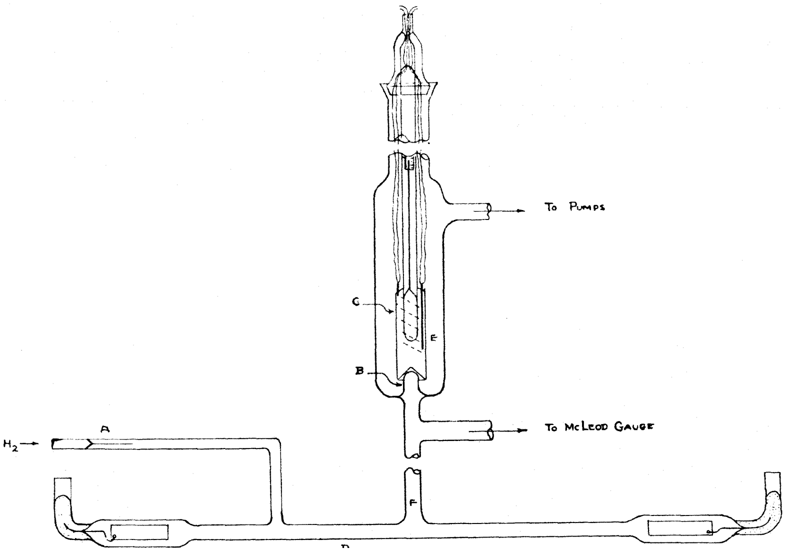

Fig. 1.—Diagrammatic sketch of apparatus.

This method employs the study of rates of effusion reported by one of us.[2] It was shown in this paper that the formula for the rate of effusion of a pure gas through a small hole could be employed experimentally to de-

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[1] This paper is an abstract of a thesis presented by L. Covell Copeland in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Johns Hopkins University.

[2] Weide and Bichowsky, THIS JOURNAL, 48, 2529 (1926).

termine the percentage of thermal dissociation. As the present work deals with hydrogen dissociated in a discharge tube, the development of the final formula is given again.

The number of molecules of hydrogen, N_N, passing through a hole of area s in t seconds is[3]

$$N_N = N_0\, St\, P_N/\sqrt{2\pi K M_{\mathrm{H}_2} T_N} \qquad (1)$$

where N_0 is Avogadro's number, M_{H_2} is the mass of a hydrogen molecule, P_N is the pressure on the high pressure side of the small hole, and T_N is the temperature of the hole. If the gas is partially dissociated the number of particles of dissociated gas will be equal to the sum of the molecular and atomic particles. It is most practical to measure the flow of gas before it is dissociated. Under conditions of equilibrium and no dissociation the number entering the apparatus is equal to the number passing through the small hole. When the gas is partially dissociated the number of molecules entering the apparatus under conditions of equilibrium is equal to the number of hydrogen molecules plus one-half the number of hydrogen atoms passing through the small holes. This number is N_D

$$N_D = N_{\mathrm{H}_2} + \frac{1}{2}N_{\mathrm{H}} = \frac{N_0\, St}{\sqrt{2\pi K T_D}}\left(\frac{P_{\mathrm{H}_2}}{\sqrt{M_{\mathrm{H}_2}}} + \frac{1}{2}\,\frac{P_{\mathrm{H}}}{\sqrt{\frac{M_{\mathrm{H}_2}}{2}}}\right) \qquad (2)$$

Dividing equation (1) by equation (2) and substituting

$$P_D - \left(1 - \frac{1}{2}\sqrt{2}\right) P_{\mathrm{H}} \text{ for } P_{\mathrm{H}_2} + \frac{1}{2}\sqrt{2}\, P_{\mathrm{H}}$$

(where P_D is the total pressure of the dissociated gas)[4] and solving for P_{H} equation (3) is obtained

$$P_{\mathrm{H}} = 3.41\left(P_D - P_N \frac{N_D}{N_N}\sqrt{\frac{T_D}{T_N}}\right) \qquad (3)$$

It is shown experimentally that, by using a capillary to control the rate of flow of hydrogen, the rate of flow when the gas was dissociated N_D was equal to the rate of flow when there was no dissociation N_N. Also, the temperature of the small holes did not vary more than 5°K. Therefore the fraction $(N_D/N_N)\sqrt{T_D/T_N}$ may be set equal to one and formula (3) reduces to

$$P_{\mathrm{H}} = 3.41(P_D - P_N) \qquad (4)$$

If α is used to represent the percentage of dissociated gas, 2α equals P_{H} and $1 + \alpha = P_D$

$$\frac{2\alpha}{1+\alpha} = \frac{P_{\mathrm{H}}}{P_D} = 3.41\left(1 - \frac{P_N}{P_D}\right)$$

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[3] Jeans, "The Dynamical Theory of Gases," Cambridge University Press, Cambridge, England, 4th ed., 1925, p. 121.

[4] $P_D = P_{\mathrm{H}_2} + P_{\mathrm{H}}$
$P_D - Pa = P_{\mathrm{H}_2}$
$P_D - P_{\mathrm{H}} + \frac{1}{2}\sqrt{2}\,P_{\mathrm{H}} = P_D - \left(1 - \frac{1}{2}\sqrt{2}\right)P_{\mathrm{H}} = P_{\mathrm{H}_2} + \frac{1}{2}\sqrt{2}\,P_{\mathrm{H}}.$

Solving for *a* the percentage of atomic hydrogen flowing through the small hole is obtained.

Apparatus

The capillary **A** served to control the rate of flow of hydrogen into the apparatus. An automatic electrolytic hydrogen generator fitted with nickel electrodes and a 30% solution of potassium hydroxide as electrolyte was used as a source of moist hydrogen. As this generator, because of its automatic action, used only sufficient current to equalize the flow of hydrogen through the capillary, it was possible to use a second hydrogen generator connected in series with the first to measure the rate of flow. The discharge tube D was a Wood's tube,[5] so constructed that it could be immersed in a water-bath. The tube received its energy from an alternating current transformer delivering about 1000 volts and 0.2 of an ampere. The dissociated gas left the discharge tube through F, which was a section of one cm. tubing 25 cm. long. The tube F terminates in the small hole system B which was ring-sealed into the calorimeter jacket E. To obtain the maximum percentage of dissociation, the pressure in the discharge tube was maintained below 0.5 mm. of mercury. Since the theory on which this work is based demands that the small hole be small in comparison with the mean free path of the gas, the size of the hole was seriously limited.

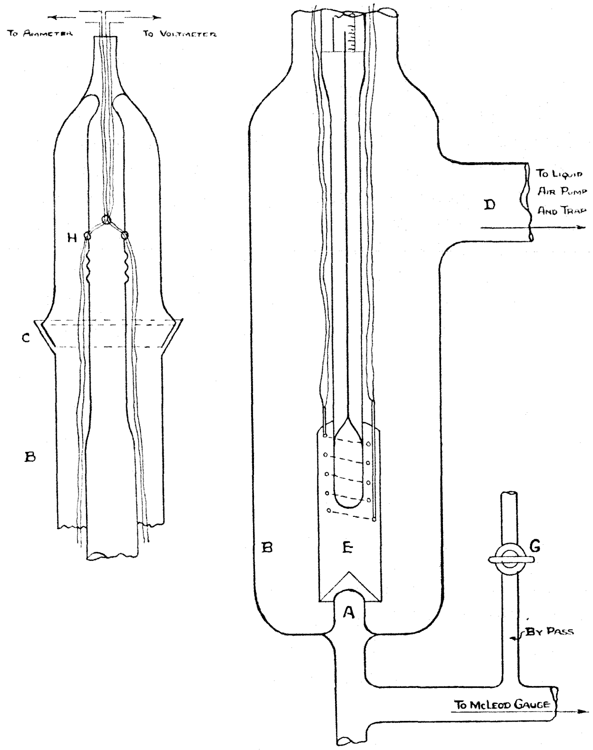

Fig. 2.—Sectional diagram of calorimeter and jacket.

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[5] Wood, *Phil. Mag.*, 42,729 (1921); *Proc.* Roy. *Soc.* (*London*), 102, 1 (1923).

In order to obtain a sufficient flow of gas to give the desired accuracy in the calorimetric data, it was necessary to use a multiple system of small holes. The arrangement used consisted of nine small holes with diameters between 0.125 and 0.25 mm. These holes were constructed by rounding off one end of a piece of one cm. pyrex tubing which was then blown out until it was thin enough to work readily in a soft air flame. This thin wall was backed with sealing wax and the holes, first countersunk with a diamond drill, were completed with a drill made from 0.125 mm. tungsten wire. The sealing wax was removed by dissolving it in alcohol.

Figure 2 is a sketch of the calorimeter jacket and the calorimeter. B is the calorimeter jacket, which consisted of an 18-cm. length of 6-cm. tubing surmounted by a length of 4-cm. tubing containing a ground glass joint C. From one side of the calorimeter jacket a 2.5 cm. piece of tubing, D, served to conduct the gases through a liquid air trap to the pumps. A stopcock G was installed for by-passing the gas around the calorimeter. The calorimeter E was constructed of a cylinder of platinum foil 9.5 cm. long and 2 cm. in diameter. This cylinder was closed at the bottom end by a platinum foil cone and sealed around the bulb of a Beckmann thermometer by Wood's metal. The Beckmann and calorimeter were supported from the top by means of a graded seal H, one end of which was sealed to the Beckmann and the other end ring-sealed to the upper portion of the ground glass joint as shown in Fig. 2. This means of support was adopted because it afforded the minimum amount of heat loss through conduction. The ground glass joint facilitated the removal of the Beckmann and calorimeter to set the Beckmann. For the purpose of determining the heat capacity of the Beckmann and calorimeter, a coil of nichrome wire was immersed in the Wood's metal of the calorimeter at the time the calorimeter was assembled. Two fine copper enameled wires connected the resistance unit through a Weston milliammeter to a 6-volt storage battery. Two other wires were connected to a Weston 3-volt voltmeter. The calorimeter jacket was covered with asbestos paper as far as the ground glass joint. A slit was cut from this covering in order to read the Beckmann. Pressure measurements were made with a McLeod gage which was read with a cathetometer.

Experiments

It was found that two hours of continuous discharge were necessary to give a steady pressure in the discharge tube. The pressures reported here are the average of the corrected pressures observed during the third hour of a continuous run. The pressure on the low pressure side of the small hole (that is, around the calorimeter) was 0.005 mm. The temperature of the calorimeter was recorded every minute by plotting directly degrees

EXPERIMENT 1

Rate of flow of hydrogen corrected to normal temperature and pressure	10.77 cc./10 min.
Pressure in discharge tube with no current	0.24006 mm.
Pressure in discharge tube with current	0.27687 mm.

$$\frac{2\alpha}{1+\alpha} = \frac{P_H}{P_D} = \frac{3.41\ (0.27687 - 0.24006)}{0.27687} = 0.4531$$

a = 29.3 per cent. of H_2 dissociated

10.77 cc./10 min. × 0.293 = 3.155 cc. of dissociated H_2 in ten minutes

Calorimetric data = 15.03 cal./10 min.

$$\frac{22{,}412}{3.155} \times 15.02 = 100{,}900 \text{ cal./gr. mol. wt.}$$

Beckmann against time. The resulting curves were corrected for cooling effect and their calorimetric values computed from the specific heat of the calorimeter, which was found to be 7.763 cal./deg. Fig. 3 shows the temperature curves used in one experiment.

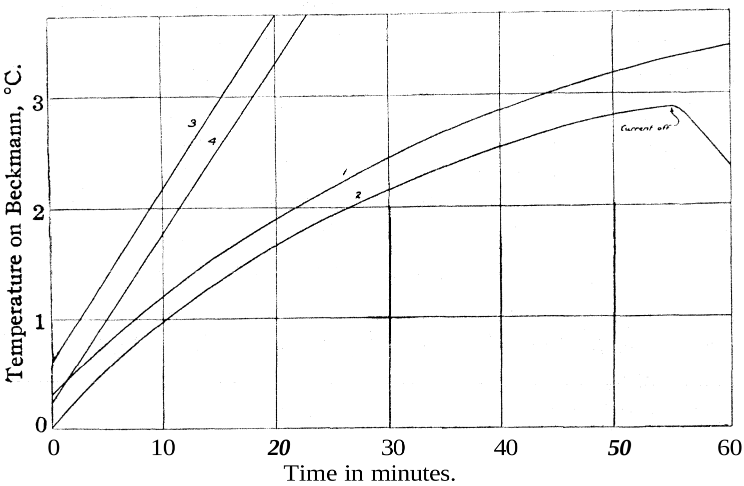

Fig. 3.—1, Temperature curve with discharge on; 2, temperature curve of calibration; 3, curve 1, corrected; 4, curve 2, corrected.

Experiment 2

Rate of flow of hydrogen corrected to normal temperature and pressure	10.10 cc./10 min.
Pressure in discharge tube with no current	0.23877 mm.
Pressure in discharge tube with current	0.27094 mm.

$$\frac{2\alpha}{1+\alpha} = \frac{p_H}{p_D} = \frac{3.41\ (0.27094 - 0.23877)}{0.27094} = 0.4049$$

$\alpha = 25.38$ per cent. of H_2 dissociated

10.10 cc./10 min. X 0.2538 = 2.56 cc. of dissociated H_2 in 10 min.

Calorimetric data = 11.8 cal./10 min.

$$\frac{22{,}412}{2.56} \times 11.80 = 103{,}100 \text{ cal./gr. mol. wt.}$$

Experiment 3

Rate of flow of hydrogen corrected to normal temperature and pressure	10.56 cc./10 min.
Pressure in discharge tube with no current	0.24289 mm.
Pressure in discharge tube with current	0.27598 mm.

$$\frac{2\alpha}{1+\alpha} = \frac{p_H}{p_D} = \frac{3.41\ (0.27598 - 0.24289)}{0.27598} = 0.40326$$

a = 25.25 per cent. of H_2 dissociated

10.56 cc./10 min. × 0.2525 = 2.66 cc. of dissociated H_2 in 10 min.

Calorimetric data = 12.6 cal./10 min.

$$\frac{22{,}412}{2.66} \times 12.6 = 105{,}810 \text{ cal./gr. mol. wt.}$$

As a check on this method a blank experiment was carried out. A piece of platinum wire gauze was inserted in the tube leading from the discharge tube to the small holes at the point F in Fig. 1. The purpose of this gauze was to associate all the atomic hydrogen before it reached the small hole system and calorimeter. The results of this experiment showed that there was no observable difference of pressure between the steady state of discharge and the steady state of no discharge, and that there was no observable heat effect in the calorimeter. We feel that these results prove that the observed pressure change in the reported experiments were due to atomic hydrogen which was completely associated by the platinum gauze, and that there was no thermal leakage from the Wood's tube to the calorimeter.

Discussion

The reported values of the heat of association of atomic hydrogen are as follows: Langmuir,[6] from the energy loss of a tungsten filament heated in hydrogen, 90,000 cal.; Frank,[7] from the energy absorbed by molecular hydrogen from electron impact, 80,000–100,000 cal.; Olsen and Glockler,[8] from a study of ionization potentials, 73,000 cal.; Wohl,[9] from the energy of a detonating gas mixture, 96,000 cal.; Bodenstein and Jung,[10] from calculations on the heat of formation of hydrogen bromide investigated by Herzfeld,[11] 107,000 cal.; Whitmer,[12] from band spectra of hydrogen, 100,100 cal.; Dieke and Hopfield,[13] also from band spectra of hydrogen, 101,000 cal.; Condon,[14] from a study of wave mechanics, 101,400 cal.; this method average, 105,270 cal.

The possible experimental errors introduced by the limits of the accuracy of the recorded data are as follows:

Source of error	Possible % error in results	Source of error	Possible % error in results
Rate of flow of hydrogen	0.25	Calibration of calorimeter	1.25
Steady state pressures	3.00	Limiting experimental error	3.28
Temperature rise of calorimeter	0.34	Experimental deviation from the mean	1.1

The following theoretical assumptions are involved in this method. (I) The gas on the high pressure side of the small hole has a distribution of velocity that will permit the use of equation (1). (II) The observed pres-

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[6] Langmuir, THIS JOURNAL, 36, 1708 (1914); 37, 417 (1915).

[7] Frank, *Physik. Z.*, 22, 467 (1921).

[8] Olsen and Glockler, *Proc. Nat. Acad. Sci.*, 9, 122 (1923).

[9] Wohl, *Z. Electrochemie*, 30, 49 (1924).

[10] Bodenstein and Jung, *Z. physik. Chem.*, 121, 127 (1926).

[11] Herzfeld, *Ann. Physik*,, 59, 635 (1919).

[12] Whitmer, *Proc. Nat. Acad. Sci.*, 12, 238 (1926).

[13] Dieke and Hopfield, *Z. Physik*, 40, 239 (1926).

[14] Condon, *Proc. Nat. Acad. Sci.*, 13, 469 (1927).

sure change is due solely to the percentage of monatomic hydrogen passing through the small hole. (III) The calorimeter records the total energy of recombination of the dissociated gas that passes through the small holes and only this energy.

Since the flow of gas through the apparatus imparts an added velocity to the gas in the direction of the hole, the validity of assumption (I) is brought into question. One cc. of hydrogen, measured at atmospheric pressure, flowing through a tube 0.85 cm.^{2} in cross section, at a pressure of 0.25 mm. has a velocity of about 70 cm./sec. Since the average velocity of a hydrogen molecule at 300°K. is about 210,000 cm./sec., this superposed unidirectional flow can have little effect on the distribution of velocities. Of even less importance is the effect on distribution of velocities of the recombination of the hydrogen atoms on the walls and through ternary collisions in the region in front of the small holes. The rate of recombination of monatomic hydrogen is not known but supposing as an upper limit that it is proportional to the concentration of atomic hydrogen, and supposing the gas leaving the discharge tube to be pure atomic hydrogen, about 1.5% of the atomic hydrogen would combine in the cm. in front of the holes. The amount passing through the tube is 1 cc. of H_2 or 2 cc. of H per minute. The limiting rate of combination is $2.7 \times 10^{19} \times 0.25/760 \times 0.015 \times 2/60 = 4.4 \times 10^{12}$ atoms per sec. But the total number of collisions of the hydrogen atoms per cc. per sec. at these pressures is of the order of $2 \times 10^{29} \times 0.25/760 = 6.6 \times 10^{25}$; therefore the proportion of collisions resulting in chemical reaction is negligible.

Assumption (II) requires that under the conditions of this experiment there is no H_3 or any species of hydrogen other than H and H_2.

Recent experiments[15] seem to render improbable the existence of H_3 under these conditions. If it were present our results would have been lowered because of the higher concentration of H present than was assumed. They would also have to be varied because the heat reaction $H + H_2 = H_3$ is small. The two partial corrections would tend to cancel. That there is no pressure drop due to some effect of the discharge other than that due to a gas which recombines on platinum is shown by the blank experiment.

Although a known impurity of about 3% of water vapor was present, the probability of dissociated water vapor in an atmosphere of hydrogen, at a distance of 25 cm. from the discharge tube is exceedingly small. Since the same amount of water vapor passed the small holes during discharge and when there was no discharge, it had no effect on the pressure measurements.

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[15] (a) Paneth, Kiever and Petros, *Z. Electrochem.,* **33,** 102 (1927); (b) Smallwood and Urey, THIS JOURNAL, 50, 620 (1928); (c) Bach, *Ber.,* **58B,** 1388 (1926); (d) Scanavy-Grigoriewa, *Z. anorg. allgem. Chem.,* 159, 55 (1927).

Assumption (III) requires that there be no heat effect not due to combination of hydrogen on the calorimeter. This is proved by the blank experiment. It also requires that all the monatomic hydrogen passing through the small holes recombine on the platinum calorimeter. The mean free path at the pressures in the calorimeter is long enough to insure that every hydrogen atom will strike the calorimeter at least once. From the geometry the probable number of collisions is at least 3. The coefficient of recombination of hydrogen atoms on a platinum surface is not known but all qualitative information indicates it is very high. If it is above 80%, the error introduced is less than 1%. Such incomplete recombination would mean that our value was too low.

This determination was made at constant pressure. The corresponding value at constant volume would be some 600 calories smaller.

Summary

A new direct method for the determination of the heat of formation of molecular hydrogen has been described. The mathematical theory and a description of the apparatus have been given.

The results of three experiments and one blank determination have been presented with a discussion of the possible experimental and theoretical errors.

The value of the heat of formation of molecular hydrogen has been determined by this method as 105,000 ± 3500 calories.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. I. PREPARATION AND STANDARDIZATION OF SOLUTIONS. DETERMINATION OF CALCIUM

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Introduction

The use of ceric salts as oxidizing agents has been suggested by a number of authors. Lange[2] in referring to the oxidizing properties of ceric sulfate recommends it as a volumetric reagent; Sonnenschein[3] suggests it instead of permanganate for the titration of iron; A. Job[4] speaks of the stability and strong oxidizing properties of acid solutions of ceric salts and of their possible use in cases where permanganate is not applicable as in the esti-

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry

[2] Lange, *J. prakt. Chem.*, *82*, 129 (1861).

[3] Sonnenschein, *Ber.*, 3, 631 (1870).

[4] Job, *Compt. rend.*, 128, 101 (1899).

mation of oxalochlorides, the excess of the reagent being determined with hydrogen peroxide. This last author states that the oxidizing solution may be prepared from ordinary commercial cerium compounds as the presence of the other monazite metals has no influence on results. G. Barbieri[5] discusses the volumetric determination of nitrous acid by means of tetravalent cerium, the factor of which is determined iodimetrically or with hydrogen peroxide. He remarks that ceric compounds are reduced by hydrazine and hydroxylamine salts in the cold. Sommer and Pincas[6] find that salts of quadrivalent cerium immediately effect the complete oxidation of hydrazoic acid in neutral or acid solution, and Martin[7] has developed an iodimetric method for determining the excess of ceric sulfate used in this oxidation. Benrath and Ruland,[8] in a paper on the oxidizing action of ceric sulfate, discuss the oxidation of a number of organic compounds as tartaric acid, oxalic acid, anthracene, hydrazine, hydroxylamine, as well as sodium thiosulfate, sulfurous acid, hypophosphorous acid. Ceric salts have been used in the electrolytic oxidation of organic compounds and a number of volumetric methods for the estimation of cerium have been worked out.[9] No one, however, has yet used ceric salts in the direct titration of reducing agents.[10]

An extensive development of analytical methods based upon the use of ceric salts as volumetric reagents would have been difficult before the advent of the potentiometric method of determining an end-point. Though a visual change or an internal indicator may be used in some cases, the end-point in many of the titrations must be determined electrometrically. Since the oxidation potential of the most powerful oxidizing agents such as that of permanganate in acid solution is very close to that of ceric compounds in a similar medium,[11] the latter should prove to be very strong oxidizing agents and should behave in many reactions in a manner similar to permanganate. A ceric salt has, however, one great advantage, namely, that only trivalent cerium can be formed in its reduction, whereas with permanganate several reduction products are possible and it is not always easy to avoid the formation of more than one of these in a given reaction. Ceric salts may be used in solutions containing a high concentration of

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[5] Barbieri, *Chem.-Ztg.*, 29, 668 (1905).

[6] Sommer and Pincas, *Ber.*, 48, 1963 (1915).

[7] Martin, THIS JOURNAL, 49, 2133 (1927).

[8] Benrath and Ruland, *Z. anorg. allgem. Chem.*, 114, 267 (1920).

[9] Lessnig, *Z. anal. Chem.*, 71, 161 (1927), gives a brief summary of the methods for cerium.

[10] After these papers were submitted to THIS JOURNAL, a paper appeared by Furman, THIS JOURNAL, 50, 755 (1928), in which he showed that ceric sulfate could be standardized against oxalate or ferrous sulfate in sulfuric acid solution. The authors' results confirm the accuracy of these methods and considerably extend the usefulness of these reactions.

[11] Tomiček, *Rec. trav. chim.*, 44, 410 (1925).

hydrochloric acid and are very stable toward heat, while the use of permanganate under such conditions is almost always out of the question. The authors have therefore made a systematic study of ceric salts as oxidizing agents in volumetric analysis, the results of which will appear in a series of papers.

Experimental

Preparation of Ceric Sulfate

The supply of U. S. P. cerous oxalate available was found by Metzger's bismuthate method[12] to contain 48.22% of CeO_2 in the ignited oxide. While a pure cerium compound was not necessary for our purpose because no interference from the other rare earths was to be expected, it seemed better to use material containing a higher percentage of cerium. On the other hand, a material not too pure has certain advantages: a mixed oxide of the rare earths containing about 85% of CeO_2 is attacked readily by sulfuric acid, sp. gr. 1.5, with the formation of ceric sulfate, while a very pure sample of CeO_2 must be treated with concentrated sulfuric acid to obtain the sulfate.[13] The pure oxide is a relatively expensive reagent, but a ceric oxide containing other rare earths is inexpensive.

A slight modification of Roberts' permanganate process[14] for concentrating cerium in a rare earth mixture was used. The solution of the nitrates, diluted considerably with water, was heated to boiling, stirred mechanically and treated with sodium carbonate solution until a slight permanent precipitate was formed. This was dissolved in nitric acid, added drop by drop, and to the boiling hot liquid a solution, 0.25 molar in potassium permanganate and 1 molar in sodium carbonate, was added until a fair excess of permanganate was present. By this procedure all of the cerium was precipitated as dioxide along with some of the other rare earth oxides. Roberts' directions were followed in converting these oxides into chlorides and subsequently into oxalates. A considerable quantity of material was worked up by this method and the chloride solutions were combined and stirred thoroughly so that the entire oxalate precipitate would be of the same composition. The ignited oxides from this oxalate contained 85.1% of CeO_2. When the oxalate was ignited at 600–625° for ten hours, slightly more than 99% of the cerium in it was converted into CeO_2. If this was dissolved in sulfuric acid, sp. gr. 1.5, diluted and titrated directly for ceric content, 91.2% of the CeO_2 in the oxide was found as ceric sulfate. While the conversion into oxide was more nearly complete at a higher temperature, the yield of ceric salt was somewhat lower.

To prepare a large amount of ceric sulfate solution, portions of the oxide, ignited at 600–625°, were treated with sufficient sulfuric acid, sp. gr. 1.5, to make the final solution 0.5 or 1 molar in acid when it was diluted sufficiently to give a 0.1 N ceric sulfate solution. This oxideacid mixture was kept at 125–130° and stirred mechanically until the pale pinkish brown oxide, which was converted first into a deep red material, became a bright yellow in color. This material was diluted almost to the volume required for a 0.1 N solution and kept at 75–80° for an hour while being stirred mechanically. It was filtered hot from the small amount of undissolved material, which appeared to be unchanged CeO_2 and was combined with similar precipitates to be worked up later. If the U. S. P. oxalate was ignited, this impure oxide dissolved readily in sulfuric acid of sp. gr. 1.3.

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[12] Metzger, THIS JOURNAL, 31, 523 (1909).

[13] Meyer and Aufrecht, *Ber.*, 37, 140 (1904); Spencer, *J. Chem. Soc*, 107, 1265 (1915).

[14] Roberts, *Am. J. Sci.*, [IV] 31, 350 (1911).

Some of this ignited oxide was treated with 95% sulfuric acid at a temperature of 150–155°, and was converted fairly rapidly into the bright yellow ceric sulfate. This, when cool, was added slowly to water at room temperature. Nearly all of the solid dissolved and the actual yield in ceric sulfate from a given weight of the ignited oxide was very nearly the same as that in the process described above. The first method was somewhat more convenient.

A further supply of 0.1 N ceric sulfate was made from C. P. CeO_2, very pale yellow in color, by treatment with concentrated sulfuric acid as described above. From the strength of the solution obtained, it was found that 98.2% of the oxide used in the process was converted into ceric sulfate.

During a three months' interval, the normality factor of this ceric sulfate solution was constant to within one part in a thousand.

Different cerium compounds were used to prepare 0.1 N ceric sulfate, the purpose being to compare the cost of a liter of these solutions. Pure ceric sulfate and pure ceric ammonium nitrate, converted into sulfate by evaporation with sulfuric acid, were out of the question because of the expense. The approximate cost of the cerium compound for a liter of 0.1 *N* solution from C. P. CeO_2 was eighty-five cents, from U. S. P. cerous oxalate ten cents. While this last material is satisfactory for the preparation of such a volumetric solution, an oxalate containing 80–85% of the theoretical quantity of CeO_2 is perhaps preferable.

Standardization of Ceric Sulfate

Since it is very desirable to use a primary standard for this purpose, a study was made of the titration of sodium oxalate in hot solution with ceric sulfate, the reaction being

$$Na_2C_2O_4 + 2Ce(SO_4)_2 = Na_2SO_4 + 2CO_2 + Ce_2(SO_4)_3.$$

Portions of a standard solution of sodium oxalate from the U. S. Bureau of Standards were acidified with sulfuric acid, heated nearly to boiling and titrated electrometrically with 0.1 N ceric sulfate prepared from the ignited oxide containing 85.1% of CeO_2. Two cc. of sulfuric acid was contained in the ceric sulfate used. In all of this work a silver chloride–platinum electrode system was used. The silver chloride electrode in 0.1 N potassium chloride was placed directly in the liquid to be titrated. The results are shown in Table I.

These data indicate that concordant results may be obtained when the volume of the solution is varied from 100–300 cc. (larger variations in volume were not studied) and when the weight of sodium oxalate is changed over wide limits. The end-point equilibrium is quite rapid if not more than 2.5 cc. of concd. sulfuric acid is present per 100 cc. of solution at the time of titration. The high result obtained in the last experiment is probably due to the low acid content of the solution. No acid was added before the titration and only 1.85 g. of sulfuric acid was present in the ceric sulfate. It is probable that not quite all of the cerous oxalate was dissolved. In the other experiments in which no acid was added, a considerable quantity of cerous oxalate precipitated on the addition of the first portion of ceric sulfate and then dissolved as more of the reagent was added.

TABLE I

EFFECT OF SULFURIC ACID

$Na_2C_2O_4$, g.	Initial vol., cc.	H_2SO_4, sp. gr. 1.83, at beginning, cc.	$Ce(SO_4)_2$, normality	Character of end-point
0.2679	200	0	0.1067	Rapid
.2679	200	5	.1067	Fairly rapid
.2679	200	10	.1067	Slow
.2679	300	0	.1067	Rapid
.2679	300	7.5	.1068	Fairly rapid
.2679	300	15	.1068	Slow
.2679	100	0	.1067	Rapid
.2679	100	2.5	.1067	Slow but usable
.2679	100	5	.1068	Too slow
.1339	300	7.5	.1067	Rapid
.5358	300	0	.1067	Rapid
.1339	300	0	.1081	Fairly rapid

Experiments showed that the equilibrium at the end-point was reached too slowly in all cases if the temperature of the solution at the end of a titration was below 70°. At or above this temperature results were as indicated in Table I.

The results were identical no matter whether the ceric sulfate solution was added slowly to the oxalate, as would be necessary in a permanganate titration, or rapidly from a pipet.

Portions of a standard solution of sodium oxalate were acidified with hydrochloric acid, heated nearly to boiling and titrated electrometrically with 0.1 N ceric sulfate. The equilibrium at the end-point was rapid in all cases. The results are shown in Table II.

TABLE II

EFFECT OF HYDROCHLORIC ACID

$Na_2C_2O_4$, g.	Initial vol., cc.	HCl, sp. gr. 1.18, at beginning, cc.	$Ce(SO_4)_2$, normality
0.2679	200	0	0.1043
.2679	200	5	.1043
.2679	200	20	.1042
.2679	200	40	.1043
.2679	200	60	.1043
.2679	100	10	.1042
.2679	300	30	.1042
.1339	300	30	.1041
.5358	300	30	.1043

It is seen that ceric sulfate may be used with no special precautions in strong hydrochloric acid solutions and thus has a decided advantage over permanganate. The end-point break in the above experiments averaged about 175–200 mv. per 0.02 cc. of 0.1 *N* ceric sulfate, and fifteen minutes after the completion of a titration not the slightest decrease in potential had occurred.

Experiments similar to those made in Tables I and II showed that as much as 60 cc. of 73% perchloric acid or 50 cc. of glacial acetic acid per 200 cc. of solution could be used instead of sulfuric or hydrochloric acid and the end-point equilibrium was rapid. The presence of even 5 cc. of concd. nitric acid in this same volume however, gave too high a value for the ceric sulfate, showing that this acid had a slight effect on the oxalate. Phosphoric and hydrofluoric acids must be absent, even if considerable hydrochloric acid is present, as they cause the formation of insoluble cerium salts. In the titration of ferrous ion in hydrochloric acid solution with ceric sulfate, which is described later, the presence of a moderate amount of phosphoric acid causes no interference, probably because this reaction is a more rapid one than the oxalate–ceric sulfate reaction. Experiments using ceric sulfate solution prepared from pure CeO_2 gave the same results.

Since in the titration of oxalate the solution is colorless until an excess of ceric sulfate is present, the possibility of using a visual end-point was investigated. An initial volume of 200 cc., containing 10–20 cc. of concd. hydrochloric acid, was used. If an equal volume of water is taken as a comparison liquid, the slightest change in color at the end-point is easily seen. A blank determination made at 70° on 200 cc. of water containing 20 cc. of concd. hydrochloric acid and 3--3 cc. of concd. sulfuric acid (the volume in the ceric sulfate added) showed that 0.05 cc. of 0.1 *N* ceric sulfate was required to give a pale yellow color. Unless sulfuric acid was added, the ceric sulfate was reduced. When this amount was subtracted from the volume of ceric sulfate used in a titration the normality corresponded exactly to that obtained electrometrically.

Quantitative results were obtained in the reverse titration of ceric sulfate with sodium oxalate in hot solution when as much as 5 cc. of concd. sulfuric acid was present per 200 cc. of solution. If more sulfuric acid was used, the equilibrium at the end-point was too slow. Twenty-five cc. of perchloric acid (73%) or 5–20 cc. of concd. nitric acid in the same volume gave quantitative results with a fairly rapid end-point equilibrium. Hydrochloric acid had a reducing effect on the ceric sulfate present in the hot solution. The end-point breaks amounted to 150–200 mv. per 0.03 cc. of 0.1 N sodium oxalate except in the nitric acid solutions where they were of about half this magnitude. It was found that this electrometric titration with oxalate could be used after a bismuthate oxidation,[12] but the equilibrium in the region of the end-point was quite slow, due to the large amount of acid present.

Iodine Chloride as Catalyst

Later work which showed the value of certain iodine compounds as catalyst in the reaction between arsenite and ceric salt[15] suggested the

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[15] To be described in a later paper of this series.

possibility of titrating oxalate at room temperature in the presence of such a catalyst. It was found that the titration of oxalate in hydrochloric acid solution containing iodine chloride proceeded rapidly and quantitatively at room temperature. Iodine chloride was chosen although iodide or iodate worked equally well, because it necessitated no blank correction in the volume of ceric sulfate used, since the final form of the catalyst in all cases was iodine chloride. The catalytic action of iodide or iodate seemed a little slower than that of iodine chloride and the blank required for either was an objection.

The action of the catalyst in this reaction is not clear. It was found that iodine chloride is not reduced at all by oxalate in hydrochloric acid solution in thirty minutes, nor does it catalyze at room temperature the action of oxalate in hydrochloric acid solution with (1) potassium permanganate, **(2)** potassium dichromate or **(3)** potassium iodate. Its catalytic action seems to be confined to the ceric salt titration and this suggests the possibility that the ceric ion is an important factor, since cerous salt was found not to catalyze the action between iodine chloride and oxalate. This same conclusion was drawn from work with the arsenite titration. This subject is being investigated,

The iodine chloride solution was prepared by dissolving **0.279** g. of potassium iodide and 0.178 g. of potassium iodate in **250** cc. of water and adding all at once **250** cc. of concd. hydrochloric acid.[16] The solution thus obtained was **0.005** M in iodine chloride. It was adjusted electrometrically by adding the proper amount of dilute potassium iodide or iodate.

Measured portions of a standard solution of sodium oxalate were acidified with hydrochloric acid. Iodine chloride was added and water to a total volume of **100** cc. The end-point was determined electrometrically. The results are shown in Table III.

TABLE III

TITRATION OF OXALATE, IODINE CHLORIDE AS CATALYST

$Na_2C_2O_4$, 0.1 *N*, cc.	HCl, sp. gr. 1.18, at beginning, cc.	ICl, cc.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Character of end-point
10	10	10	9.98	Slow
10	15	10	9.99	Rapid
10	25	10	9.98	Rapid
10	20	5	9.99	Rapid
10	15	20	9.99	Rapid
50	15	10	49.94	Rapid
50	25	10	49.90	Slow
10	20	10 cc. 0.0025 M KI	10.49	Rapid
10	15	5 cc. 0.0025 M KIO_3	9.54	Fairly slow

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[16] G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Company, New York, 1926, pp. 8, 9.

In the lower acid range (first experiment) the reaction is at first more rapid than in the higher acid range (third experiment), but the equilibrium at the end point is slower. The addition of 15–25 cc. of concd. hydrochloric acid per 100 cc. of solution, not considering the acid present in the iodine chloride solution, gives the most favorable conditions for a titration. The values of the blanks in the last two experiments, +0.49 cc. and −0.46 cc., correspond very closely with the volumes of ceric sulfate theoretically required, +0.48 cc. and −0.46 cc., to convert either of the catalysts used into iodine chloride. The potential at the beginning of a titration is approximately 625–675 mv., but drops to 400–450 mv. during the addition of the first few cubic centimeters of oxidizing solution. At the end-point the break in potential averaged 200–250 mv. per 0.03 cc. of 0.1 N ceric sulfate.

Methylene blue has been proposed by Sinnatt[17] instead of starch in iodimetric titrations, and Atack[18] has discussed its use as a volumetric reagent in oxidation-reduction reactions. This dye was found to give an excellent end-point in the titration of oxalate with ceric salt in the presence of iodine chloride as catalyst, provided that certain rather narrow experimental conditions were maintained.

During this titration the solution is pale yellow, and as the end-point is approached becomes a deeper yellow, due to the presence of free iodine. As the last portion of ceric sulfate (0.2–0.3 cc.) converts this into iodine chloride, the yellow color gradually fades out. In a titration in which the end-point equilibrium is rather slow, the electrometric break in potential is indicated when the solution is still somewhat yellow and two or three minutes or longer may be required for this color to bleach out. The color disappears much more quickly when conditions are such that the end-point equilibrium is rapid. Experiments have shown that methylene blue cannot be added until within 0.4 cc. of the end-point, and the color change is much sharper if it is not added until within 0.2–0.3 cc. Therefore conditions for a rapid end-point equilibrium must be chosen. When 2 drops of the indicator are added to a pale yellow solution, the solution turns green, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade. Under some conditions the entire solution will not become pink, in which cases, as well as in the above, the end-point is taken as the reading for the last drop which caused the appearance of any pink color in the solution.

Measured portions of a standard solution of sodium oxalate were taken. Iodine chloride and hydrochloric acid were used after sufficient water had

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[17] **Sinnatt,** *Analyst,* 35, 309 (1910); 37,252 (1912).

[18] **Atack, J.** *Soc. Dyers and Colourists,* 31,183 (1915).

been added to make the total volume of the solution 100 cc. at the time of titration. Two drops of a 0.1% solution of methylene blue in water were added when within 0.2–0.3 cc. of the end-point. The results are shown in Table IV.

TABLE IV

TITRATION OF OXALATE—METHYLENE BLUE INDICATOR

$Na_2C_2O_4$, 0.1 *N*, cc.	**HCl**, sp. gr. 1.18, at beginning, cc.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Character of end-point color change
10	15	10.01	Satisfactory
10	20	9.98	Excellent
10	25	9.99	Excellent
10	35	?	Not satisfactory
25	10	24.99	Fairly satisfactory
25	15	24.97	Satisfactory
25	20	24.99	Excellent
25	25	?	Not satisfactory
50	20	49.83	Satisfactory
50	15	49.90	Excellent

The amount of iodine chloride was varied, but 10 cc. was found to give the best results.

Titration of Ferrous Iron with **Ceric** Sulfate

To be able to compare the titrations of ceric sulfate against (1) oxalate and (2) ferrous sulfate as a further check on this method of standardizing a ceric salt, the conditions necessary for the ferrous iron–ceric salt reaction were determined.

$$2FeSO_4 + 2Ce(SO_4)_2 = Fe_2(SO_4)_3 + Ce_2(SO_4)_3$$

The same volume of ceric sulfate was required in each of 6 titrations of 40 cc. of 0.1 N ferrous sulfate in which the volume was varied from 100–300 cc. and the sulfuric acid, sp. gr. 1.83, from 0–25 cc. per 100 cc. of solution. The end-point was determined electrometrically; the end-point equilibrium was rapid in every case and the break in potential amounted to 250–300 mv. per 0.02 cc. of 0.1 N ceric sulfate.

Similar results were obtained when hydrochloric or perchloric acid was used. With as much as 40 cc. of concd. hydrochloric acid or 40 cc. of perchloric acid (73%) per 100 cc. of solution, the end-point equilibrium was rapid and the break in potential large. Nitric acid, however, was detrimental, and the presence of 5 cc. of it per 100 cc. of solution caused a decided decrease in the volume of ceric salt used.

The titration of ceric salt with ferrous sulfate[19] went smoothly when considerable sulfuric or perchloric acid was present. Five cc. of concd. hydrochloric acid per 100 cc. of solution containing 25 cc. of 0.1 *N* ceric

[19] Since the completion of this work an article by Someya, *Z. anorg. allgem. Chem.*, 168, 56 (1927), has appeared in which the electrometric titration of ceric sulfate with ferrous sulfate is described.

sulfate caused no interference if the titration was made without delay. If the solution was allowed to stand for five to fifteen minutes before titration, the reducing action of the acid became evident. Quantitative results were obtained with the use of as much as 30 cc. of concd. nitric acid per 100 cc. of solution.

Comparison of Standardizations against Oxalate and Iron

A weight buret was used for the ceric sulfate solution. The samples of sodium oxalate were from the Bureau of Standards and the impurities in the electrolytic iron had been accurately determined. In the titrations of oxalate, in one series, 0.35–0.40-g. samples were dissolved in 200 cc. of water, 10 cc. of concd. hydrochloric acid added and the solutions heated nearly to boiling before titration; while in the second series the samples were dissolved in 75 cc. of water, 15 cc. of concd. hydrochloric acid and 10 cc. of iodine chloride added before titration. In the third series, the samples of electrolytic iron were dissolved in hydrochloric acid, any ferric chloride reduced with a slight excess of stannous chloride, the cooled solution diluted to 150 cc., 10 cc. of saturated mercuric chloride solution added and the solution titrated.[20] The electrometric method was used in all cases. During the titration an atmosphere of carbon dioxide was maintained above the solution to prevent any oxidation of the ferrous iron by air.. Later work showed that if this precaution was not taken there was an error of approximately one part in a thousand.

TABLE V

WEIGHT NORMALITY OF CERIC SULFATE BY DIFFERENT METHODS

Against	(1) Electrolytic Fe, 99.97% Fe	(2) $Na_2C_2O_4$ in hot soln.	(3) $Na_2C_2O_4$ at room temp. with ICl as catalyst
	0.09410	0.09410	0.09406
	.09414	.09416	.09409
	.09408	.09407	.09409
	.09409	.09406	.09404
Average =	.09410	.09410	.09407

Fig. 1 shows typical curves for the titration of oxalate and of ferrous iron with ceric sulfate. The results are expressed in terms of a platinum-1 N calomel electrode system.

Determination of Calcium with Ceric Sulfate

It is obviously possible to use ceric sulfate like permanganate for the volumetric determination of calcium. A. Job[4] has referred to the estimation of oxalic acid in oxalochlorides by addition of excess of ceric salt solution, the excess being determined with hydrogen peroxide, but he gives no experimental data. Benrath and Ruland[8] in a study of the oxi-

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[20] The stannous chloride reduction method for iron followed by titration with ceric sulfate is described in paper II of this series.

dizing action of ceric sulfate state that oxalic acid is oxidized to carbon dioxide and that sulfuric acid and normal sulfates retard the reaction. Since the gravimetric determination of calcium oxide by precipitation as oxalate and ignition in air at 475–550° to carbonate[21] is a very accurate method, the results obtained in this way were compared with those obtained by volumetric titration with ceric sulfate.

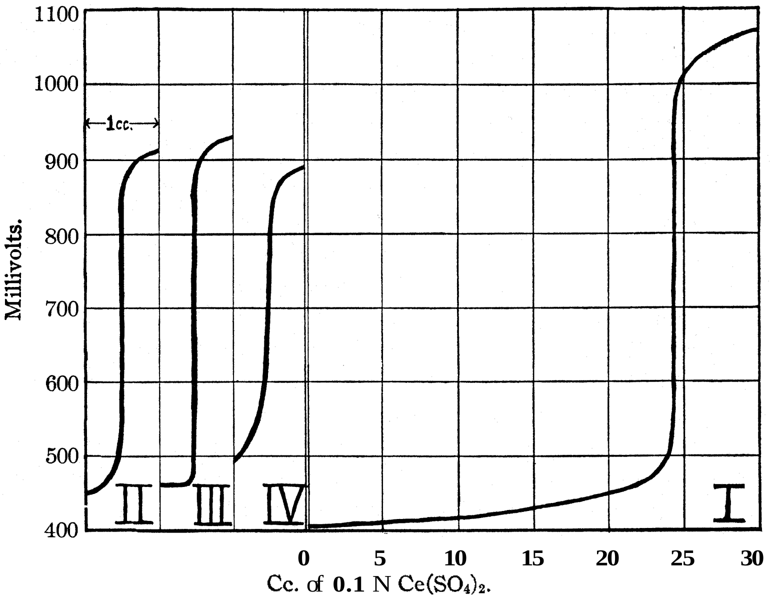

Fig. 1.—Curve I.—25 cc. of 0.1 N $Na_2C_2O_4$ titrated with 0.1 N $Ce(SO_4)_2$; 3 cc. of concd. H_2SO_4 in initial vol. of 200 cc. Curve 11.—End-point in titration of 0.1 *N* $FeSO_4$ with 0.1 N $Ce(SO_4)_2$; 15 cc. of concd. HCl in initial vol. of 100 cc. Curve 111.—End-point in titration of 0.1 N $Na_2C_2O_4$ with 0.1 N $Ce(SO_4)_2$; 15 cc. of concd. HCl in initial vol. of 200 cc. Curve IV.—Same as III but 10 cc. of 0. 005 M ICl added.

In the following analyses the standard procedure of neutralizing with ammonia a hydrochloric acid solution containing calcium and oxalate ions was followed. The precipitate was collected in a filtering crucible and ignited to carbonate in a muffle at 500–525°. In the volumetric method the precipitate was washed into a beaker with water and the paper then washed thoroughly with dilute hydrochloric acid (60 cc. of water + 10 cc. of HCl) and finally with water. The solution was diluted to 200 cc., heated nearly to boiling and titrated either electrometrically or to a visual end-point with ceric sulfate which had been standardized electrometrically against sodium oxalate. Iodine chloride was not used as a catalyst, though such a method would be equally applicable.

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[21] A method tested in this Laboratory but not yet published.

TABLE VI

SUMMARY OF ANALYSES FOR CALCIUM OXIDE

Sample	Percentage of CaO Titration with $Ce(SO_4)_2$ Electrometric	 Visual	 Weighing as $CaCO_3$
1 Iceland Spar	55.93	55.96	55.97
	55.92	55.93	55.99
	55.93	55.94	56.00
Average	55.93	55.94	55.99
2	26.60	26.64	26.65[a]
	26.59	26.62	...
	26.66	...	...
	26.60	...	
Average	26.61	26.63	26.65[a]
3	20.00	19.94	19.94[a]
	19.97	20.01	...
	20.03	...	...
Average	20.00	19.97	19.94[a]

[a] These values represent an average of accurate analyses made gravimetrically by another person.

Summary

1. A solution of ceric sulfate is easily prepared by dissolving in sulfuric acid CeO_2 obtained by igniting the oxalate. Pure material is not necessary as the other rare earths do not interfere in oxidation-reduction reactions.

2. This reagent is in some cases a stronger oxidizing agent than permanganate in acid solution and has a number of advantages over the latter: only one valence change is possible, namely, from $Ce^{++++} \longrightarrow Ce^{+++}$; it may be used in a solution containing a high concentration of hydrochloric acid and is stable toward heat. The normality factor of the solution remains constant over a long period.

3. Ceric sulfate may be accurately standardized against sodium oxalate in hot sulfuric, hydrochloric or perchloric acid solution, the end-point being determined either electrometrically or visually by a change from colorless to yellow. The titration of ceric salt with oxalate is quantitative in hot sulfuric, perchloric or nitric acid solution.

4. The oxalate titration with ceric sulfate may be carried out with the same accuracy at room temperature by the use of iodine chloride as catalyst. The end-point is determined either electrometrically or with methylene blue as internal indicator.

5. Ferrous iron may be determined volumetrically in sulfuric, hydrochloric or perchloric acid solution with ceric sulfate. The reverse titration proceeds quantitatively in a sulfuric, perchloric or nitric acid solution.

6. A method for calcium has been developed, based upon precipitation

as oxalate, solution in hydrochloric acid and titration with standard ceric sulfate.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. II. DETERMINATION OF IRON

BY H. H. WILLARD AND PHILENA YOUNG[1]

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The possibility of titrating ferrous iron with ceric sulfate has been investigated by the authors[2] and has been found to give quantitative results in either hydrochloric, sulfuric or perchloric acid solution. Furman[3] has also studied this reaction in sulfuric acid solution. It seemed important to study the application of this titration to the analysis of iron ores in which the iron was reduced in hydrochloric acid solution with stannous chloride, the excess of the latter being removed with mercuric chloride, because some of the present methods for titrating the iron after such a reduction have certain undesirable features. If permanganate is used as the oxidizing agent, the concentration of hydrochloric acid must be small because of its reducing action. Manganese sulfate is added[4] but even with this precaution the end-point obtained is fleeting, and some experience with the method is required for accurate results. This end-point has been determined electrometrically.[5] If the titration is made with dichromate, potassium ferricyanide may be used as an external indicator, an inconvenient process, or diphenylamine as an internal indicator,[6] the change in color being from a green to a deep blue shade. Many persons find it difficult to obtain a sharp color change in this latter case. The determination of the end-point electrometrically is very satisfactory.[7]

Experimental

A standard iron solution was made by dissolving electrolytic iron (99.97% Fe) in hydrochloric acid. The ferrous chloride was largely

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Willard and Young, THIS JOURNAL, 50, 1322 (1928).

[3] Furman, *ibid.*. 50,755 (1928).

[4] Barnebey, *ibid.*, 36, 1429 (1914).

[5] Erich Miiller, "Elektrometrische Massanalyse," Th. Steinkopff, Dresden, 1926, pp. 152–153; Miiller and Mollering, *Z. anorg. allgem. Chem.*, *141*, 111 (1924).

[6] Knop, THIS JOURNAL, 46,263 (1924); Mehlig, *J. Chem. Education*, 3,824 (1926).

[7] Hildebrand, THIS JOURNAL, 35, 847 (1913); Kolthoff, *Chem. Weekblad*, 16, 450 (1919); Hostetter and Roberts, THIS JOURNAL, 41, 1337 (1919); Eppley and Vosburgh, *ibid.*, 44, 2148 (1922).

oxidized by the addition of potassium chlorate. To 20 cc. of this solution, containing 0.3032 g. of iron, 5 cc. of hydrochloric acid, sp. gr. 1.18, was added and the reduction carried out with stannous chloride in the usual way. The solution was cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride and the indicated volume of hydrochloric acid added, and the solution titrated with ceric sulfate which had been standardized against sodium oxalate.

TABLE I

RESULTS OBTAINED ELECTROMETRICALLY

HCl, sp. gr., 1.18, added before titration, cc.	Error, mg. Fe	Remarks
0	–0.1	Very slight HgCl ppt.
0	– .4	Heavy HgCl ppt.
15	– .2	Very slight HgCl ppt.
15	– .3	Heavy HgCl ppt.
30	– .2	Heavy HgCl ppt.
50	?	No permanent break in potential at end-point. Solvent action of HCl on HgCl and reducing action of latter probably responsible.

Experiments similar to those above, in which 35 mg. of arsenic as sodium arsenite, or 15 mg. of manganese as manganese sulfate or both, was added to the iron solution before reduction with stannous chloride, showed that neither of these elements caused any interference. Such would not be the case with arsenic in some other methods.

Since diphenylamine has been used as internal indicator in the ferrous iron titration with dichromate and the present authors have found that diphenylbenzidine gave similar results, it seemed probable that either of these indicators might be applicable in the ferrous iron-ceric sulfate titration. Such was found to be the case, and the color change at the end-point with this latter oxidizing agent was far superior in sharpness to that obtained in a dichromate titration. This might be expected because the ceric salt is a stronger oxidizing agent than dichromate and also because the change from a green chromic salt color to a deep purple is much more difficult to see than that from a colorless cerous solution to the same deep purple shade.

The standard iron solution was reduced as described above. To the 150 cc. of solution were added 15 cc. of phosphoric acid, sp. gr. 1.37 (prepared by diluting acid of sp. gr. 1.75 with an equal volume of water), the stated volumes of hydrochloric acid and 0.1% diphenylamine (d.p.a.) or diphenylbenzidine (d.p.b.), after which it was titrated with ceric sulfate which had been standardized against sodium oxalate.

In the last two experiments the volume of the solution was 400 cc. at the beginning of the titration. The data in Table II show that no blank cor-

TABLE II

RESULTS OBTAINED WITH A VISUAL END-POINT

HCl, sp. gr. 1.18, cc.	Indicator, 0.1%	Error, mg. Fe	Character of color change
0	0.8 cc. d.p.b.	−0.3	Very sharp
15	0.8 cc. d.p.b.	− .3	Satisfactory
30	0.8 cc. d.p.b.	− .3	Satisfactory
0	0.8 cc. d.p.a.	− .2	Very sharp
15	0.8 cc. d.p.a.	− .3	Satisfactory
30	0.8 cc. d.p.a.	− .3	Satisfactory
5	1.6 cc. d.p.b.	− .4	Satisfactory
5	3.2 cc. d.p.b.	− .4	Not so sharp as preceding one
5	1.6 cc. d.p.a.	± .0	Sharp
5	3.2 cc. d.p.a.	+ .8	Not so sharp
0	0.8 cc. d.p.a.	± .0	Development of color much slower
0	0.8 cc. d.p.b.	− .3	Development of color much slower

rection is required for 0.8 cc. of either indicator, the amount used to obtain a sharp end-point, but that a correction is necessary with larger amounts of diphenylamine. If the end-point in a titration is overstepped it is possible to add a slight excess of standard ferrous sulfate solution, and after a few moments titrate to the end-point with ceric sulfate. The change in color of the indicator in the reverse titration is much slower in the strong acid solution than is the development of the color with the first drop excess of ceric salt—too slow to use it in the determination of cerium.

The consistent error of 0.2–0.3 mg. iron for 0.3 g. present, or approximately one part in a thousand, appearing in Tables I and II, might easily be caused by oxidation by the air. The addition of 1 g. of cerous sulfate to the ferrous solution caused no increase in this error, so that its catalytic action, if any, is very slight. This error was found to disappear when the titrations were made in an atmosphere of carbon dioxide. A weight buret was used here. Because of the constancy of this error, it is possible in the analysis of iron ores either to standardize the ceric sulfate solution against oxalate and multiply by 1.001 or to standardize the solution against an iron ore of known value or electrolytic iron, using the same experimental technique as employed in the unknown ore analyses.

Three Bureau of Standards iron ores were analyzed and a summary of the results obtained is given in Table III. Four-tenths to six-tenths g. samples were treated with 5 cc. of water and 25 cc. of concd. hydrochloric acid, and the material kept just below the boiling boint until all of the ore was decomposed. The insoluble residue was filtered off, decomposed with hydrofluoric and sulfuric acids, and the salts remaining were taken up with dilute hydrochloric acid and returned to the main filtrate. Ore No. 29 contained so much silica that after treatment with hydrofluoric and a drop of sulfuric acids, the material was evaporated to dryness, a small amount of sodium carbonate added and the mixture fused for 3–4 minutes. The fusion was dissolved in dilute hydrochloric acid and added to the main solution. After evaporation to 10–15 cc., the solutions were heated to boiling, reduced with a slight excess of stannous chloride, cooled, diluted to 150 cc., 10 cc. of saturated mercuric chloride solution was added and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of indicator were added before the titration. In these analyses as well as in the standardization of the ceric sulfate against electrolytic iron (99.97% Fe) no carbon dioxide was used.

TABLE III

SUMMARY OF ANALYSES OF IRON ORES

Ore	Electrometric	Indicator	
		d.p a.	d p b.
B. of S. No. 27	69.21	...	69.25
69.26% Fe	69 27	..	69.26
	69.28	...	...
	69.23	...	...
B. of S. No. 26	58.57	58.54	...
58.62% Fe	58.54	58.57	...
B. of S. No. 29	55.75	55.73	...
55.75% Fe	55.80	55.70	...

Diphenylamine was found to be a much more satisfactory indicator than diphenylbenzidine. When ceric sulfate was added to an iron ore solution containing the latter indicator, a rather heavy, white precipitate formed which dissolved slowly. This difficulty was not encountered with diphenylamine.

Analyses were made of B. of S. ore No. 27, following the directions for the stannous chloride method through the fuming of the siliceous residue with hydrofluoric and sulfuric acids and the returning of this material to the main filtrate. Four cc. of concd. sulfuric acid was added to the solution and it was evaporated to fumes of SO_3 to remove all hydrochloric acid. Twenty-five cc. of water was added to the moist residue and the liquid heated a few moments until a clear solution was obtained. Pieces of pure aluminum were added and the solution was boiled for ten minutes after it had become colorless. The aluminum was removed, the solution diluted to 150 cc. and the titration with ceric sulfate made electrometrically. For the indicator method, 15 cc. of phosphoric acid (sp. gr. 1.37) and 0.8 cc. of 0.1% diphenylamine were added before the titration. With the electrometric end-point the percentage of iron found was 69.20% and with the indicator 69.24%, both of which agree very well with the B. of S. value of 69.26%.

Summary

1. Standard ceric sulfate may be used to titrate the iron in iron ores after a stannous chloride reduction in hydrochloric acid or a reduction with aluminum or zinc in sulfuric acid solution.

2. Arsenious acid does not interfere in the method.
3. The end-point in the titration may be determined electrometrically or with diphenylamine as internal indicator.
4. Analyses of three Bureau of Standards ores show that this method of titrating the ferrous iron is a very accurate one.
5. Because of the constancy of the slight error due to oxidation of the ferrous iron by air during a titration, the ceric sulfate solution may be standardized against sodium oxalate and a very small correction factor applied, or against a standard iron ore or electrolytic iron of known purity, using the same experimental technique as employed in the analyses.

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[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNICAL INSTITUTE OF COPENHAGEN]

THE ACTIVITY COEFFICIENTS OF IONS IN AQUEOUS SOLUTIONS OF NON-ELECTROLYTES

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1. Introductory

The interionic attraction theory of Debye and Hückel[2] and of Debye[3] provides a means of evaluating the electrical potential and therefore the deviations from the ideal state of the ions in a dilute solution. These deviations may be calculated in terms of the osmotic coefficient of the solvent, φ, in terms of the activity coefficient, f_i of an ion of the i^{th} sort, or in terms of the activity coefficient, f_s, of the salt itself. The results of the calculations are,

$$1 - \varphi = w\,\frac{\epsilon^2}{6DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\,n\Sigma\nu_i} \tag{1}$$

$$-\ln f_i = z_i^2\,\frac{\epsilon^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\,\Sigma n_i z_i^2} \tag{2}$$

$$-\ln f_s = \frac{\Sigma\nu_i z_i^2}{\Sigma\nu_i}\cdot\frac{\epsilon^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\,\Sigma n_i z_i^2} \tag{3}$$

These three equations have been reduced to simpler terms, as follows, by Bronsted and LaMer[4] in one of the previous papers of this series water being used as the solvent:

$$1 - \varphi = \alpha z_1 z_2\sqrt{\mu} = 0.38\,z_1 z_2\sqrt{\mu} \tag{1a}$$

$$-\log f_i = \frac{3}{2.3}\,\alpha z_i^2\sqrt{\mu} = 0.50\,z_i^2\sqrt{\mu} \tag{2a}$$

$$-\log f_s = \frac{3}{2.3}\,\alpha z_1 z_2\sqrt{\mu} = 0.50\,z_1 z_2\sqrt{\mu} \tag{3a}$$

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[1] National Research Council Fellow in Chemistry.

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

[3] Debye, *ibid.*, *24*, 334 (1923); *25*, 97 (1924).

[4] Bronsted and LaMer, THIS JOURNAL, *46*, 555 (1924).

where α is a constant depending only upon the dielectric constant of the solvent D, the Boltzmann constant k, and the absolute temperature, T. Using the values reported by Drude[5] for the dielectric constant of water at 18°, α has a value 0.380. These equations have been amply verified in solutions in which pure water was used as the solvent.[4,6]

It is evident from Equations 2 and 3 that the activity coefficient of either ion or salt varies inversely with the product of the dielectric constant of the solvent by the absolute temperature, raised to the three-halves power:

$$-\ln f \propto \frac{1}{(DT)^{3/2}} \qquad (4)$$

It cannot be said that the validity of the fundamental equations with respect to the effect of the variation of the dielectric constant has been thoroughly tested, although it has been the subject of some investigation. Several methods of varying the constant have been utilized for the purpose. Scatchard,[7] Noyes and Baxter,[8] and Nonhebel and Hartley[9] have changed it by studying the activity coefficients of hydrochloric acid, derived from electromotive force measurements, in solutions of methyl or ethyl alcohol in water, or in the pure methyl or ethyl alcohol. Their results indicate that the activity coefficients of the acid vary with the dielectric constant of the solvent in the way required by the theory, but it cannot be claimed that the agreement is better than a rough one. This may be due partly to the fact that the manner in which the dielectric constant of water changes upon the addition of alcohol is not well enough established. The dielectric constant was varied by Baxter[6d] by the simple expedient of heating the solvent, in this case pure water. This investigator studied the solubility relations of silver iodate at 75° in pure water and various solvent salt solutions and concluded that the results conformed almost completely with the Debye-Hückel limiting law up to a concentration of 0.01 *M*.

The purpose of this article is further to study the variation of the activity coefficient of a saturating salt with change in dielectric constant of the solvent. The dielectric constant was changed by the addition of ether or of varying amounts of sugar to pure water, these solutions acting as the solvents. The activity coefficients were determined by means of the effect of a solvent salt, sodium chloride, on the solubility of highly insoluble saturating salts.

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[5] Drude, *Ann. Physik.*, 59, 61 (1896).

[6] (a) Brönsted and Brumbaugh, THIS JOURNAL, **48**, 2018 (1926); (b) Noyes, *ibid.*, 46,1098 (1924); (c) Schärer, *Physik.* Z., 25, 145 (1924); (d) Baxter, THIS JOURNAL, **48**, 615 (1926); (e) LaMer, King and Mason, *ibid.*, **49**, 363 (1927); (f) LaMer and Mason, *ibid.*, 49, 410 (1927).

[7] Scatchard, THIS JOURNAL, 47, 2098 (1925).

[8] Noyes and Baxter, *ibid.*, 47, 2122 (1925).

[9] Nonhebel and Hartley, *Phil.* Mag., 50, 729 (1925).

2. Experimental

The apparatus described by Brönsted and LaMer,[4] regulated to 18 ± 0.01°, was used for the preparation of the saturated solutions. The saturating salts taken were two in number; a uni-univalent salt, croceo tetranitrodiammino cobaltiate, and a tri-univalent salt, luteo tetranitrodiammino cobaltiate. The solutions were analyzed in the manner of the previous article, brom cresol purple being used as indicator in the titration of ammonia. The solubility relations of these salts in the various solvents are given in Tables I and II. The solubility is given, with one exception, as the average of four independent determinations, of which the individual values did not differ from their mean by more than 0.25 of 1% in any case. In the majority of cases the agreement was considerably better. The concentrations in the tables are moles per liter.

TABLE I

SOLUBILITY RELATIONS OF THE UNI-UNIVALENT SALT CROCEO TETRANITRODIAMMINO COBALTIATE $(Co(NO_2)_2(NH_3)_4)(Co(NO_2)_4(NH_3)_2)$ AT 18°

Theoretical equation (water): $-\log f = 0.50\sqrt{\mu}$

Concn. solvent salt	No. of detns.	Solubility $\times 10^4$	μ	$\sqrt{\mu}$	$\log s/s_0$
(a) Solvent, Water + Solvent Salt, NaCl					
0.000	10	3.130	0.000313	0.0181	0.0000
.001	4	3.189	.001319	.0363	.0081
.OM	4	3.284	,004328	.0658	.0209
.010	4	3.412	.010341	.1017	.0374
(b) Solvent, 0.585 M Sugar Solution + Solvent Salt, NaCl					
0.000	4	3.519	0.000352	0.0187	0.0000
.001	4	3.594	.001360	,0369	.0091
.004	4	3.703	.004370	.0661	.0221
.010	4	3.844	.010384	.1019	.0386
(c) Solvent, 0.877 M Sugar Solution + Solvent Salt, NaCl					
0.0000	4	3.694	0.000370	0.0192	0.0000
.001	4	3.777	.001377	.0371	.0096
.004	4	3.903	.004390	.0663	.0239
.010	4	4.048	.010405	.1022	.0400
(d) Solvent, 1.140 M Sugar Solution + Solvent Salt, NaCl					
0.000	4	3.797	0.000380	0.0195	0.0000
.001	4	3.892	.001389	.0373	.0106
.004	4	4.033	.004403	.0665	.0261
.010	4	4.182	.010418	.1025	.0420
(e) Solvent, Water Saturated with Ether + Solvent Salt, NaCl					
0.0000	4	2.606	0.000261	0.0161	0.0000
.001	4	2.661	.001266	.0356	.0091
.004	4	2.749	.004275	.0653	.0234
.010	4	2.876	.010288	.1002	.0429

TABLE II

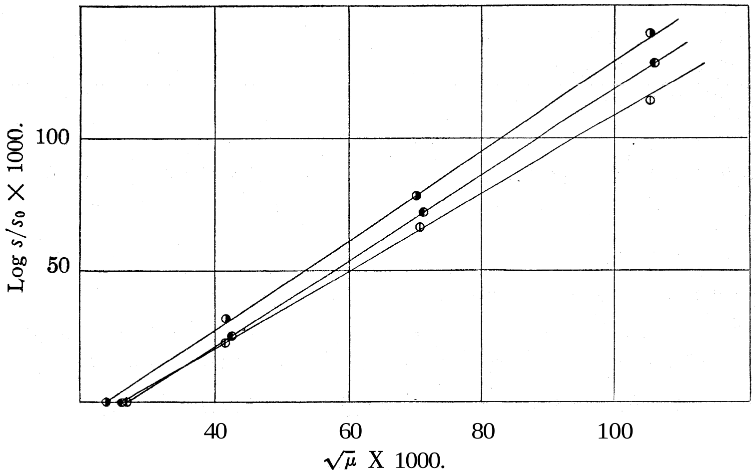
SOLUBILITY RELATIONS OF THE TRI-UNIVALENT SALT LUTEO TETRANITRODIAMMINO COBALTIATE $(Co(NH_3)_6)^{+++}(Co(NO_2)_4(NH_3)_2)_3^-$ at 18°

Theoretical equation (water): $-\log f = 1.50\sqrt{\mu}$

Concn solvent salt	No. of detns.	Solubility × 10^4	μ	$\sqrt{\mu}$	log s/s_0
(a) Solvent, Water + Solvent Salt, NaCl					
0.000	4	1.150	0.000690	0.0263	0.0000
.001	4	1.208	.001720	.0414	.0213
.004	4	1.339	.004802	.0693	.0661
.010	4	1.495	.010900	.1044	.1140
(b) Solvent, 0.877 M Sugar Solution + Solvent Salt, NaCl					
0.000	4	1.224	0.000732	0.0271	0.0000
.001	4	1.296	.001778	.0422	.0250
.004	4	1.440	.004864	.0697	.0706
.010	4	1.632	.010980	.1048	.1250
(c) Solvent, Water Saturated with Ether + Solvent Salt, NaCl					
0.000	4	1.008	0.000605	0.0246	0.0000
.001	4	1.085	,001690	.0411	.0320
.004	4	1.195	.004720	.0690	.0740
.010	4	1.381	.010830	.1042	.1368

3. Discussion of Results

The values of the logarithm of the solubility ratio, log s/s_0, obtained directly from the analytical data have been plotted against the square roots of the ionic strength and the slopes of the resulting straight lines determined. A typical plot is shown in Fig. 1, which utilizes the data of Table II.



⦶ Solvent, water; ◐ Solvent, sugar solution, 0.877 μ; ◑ Solvent, water saturated with ether.

Fig. 1.

According to equation (3a) the data of Table I(a) should be represented by the equation

$$-\log f_s = \log s/s_\infty = 0.50\sqrt{\mu}$$

The actual slope of the line is 0.446, a value which is approximately 11% lower than the theoretical. That this discrepancy cannot be considered as serious has been pointed out by Brönsted and Brumbaugh.[6a] See also refs. 6e and f, when the factors influencing the value of the constant are discussed.

The data of Table II(a), in which a tri-univalent saturating salt was used, give the slope 1.46 which corresponds very closely to the theoretical equation.

The point to be emphasized in this article is the manner in which the slope of the curve changes as the solvent is changed by the addition of cane sugar or ether to the water. Since the dielectric constants of the various sugar solutions and of water saturated with ether are known, the change in slope required by the interionic attraction theory can be calculated. A comparison of the actual change in slope produced with the theoretical is given in Tables III and IV.

TABLE III

CROCEO COBALTIATE–COMPARISON OF INCREASE IN SLOPES AS SOLVENT IS CHANGED

Solvent	D. C. (K.)[10]	D. C. (H.)[11]	D. C. (Kr.)[12]	Slope	Actual % change	Theoretical % change K.	H.	Kr.
Water	80.7	78.7	80.3	0.446	..	..	..	..
Sugar solution 0.585 M	75.8	74.5	..	.475	6.5	9.0	8.0	..
Sugar solution 0.877 M	73.5	72.7	..	.495	11.0	13.5	11.4	..
Sugar solution 1.140 M	71.5	71.0	..	.530	18.6	17.0	15.0	..
Water saturated with ether	..	..	74.5	.498[a]	11.6	..	..	10.9

TABLE IV

LUTEO COBALTIATE–COMPARISON OF INCREASE IN SLOPES AS SOLVENT IS CHANGED

Solvent	D. C.	Slope	Actual % change	Theoretical % change K.	H.	Kr.
Water	Table III	1.50	..	..	..	..
Sugar solution 0.877 M	Table III	1.66	10.7	13.5	11.4	..
Water saturated with ether	Table III	1.68[a]	12.0	..	..	10.9

[a] These slopes have not been corrected for the "salting-out effect" of the sodium chloride on the ether. The effect is within the limits of experimental error.

The dielectric constant data of Kockel and Harrington for the sugar solutions have been chosen because, in the opinion of the authors, they are the best available at the present time. That the agreement between

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[10] Dielectric constant data of Kockel, *Ann. Physik,* **77,** 417 (1925); interpolated both for temperature (18°) and concentration.

[11] Dielectric constant data of Harrington, *Phys. Rev.,* 8, 581 (1916); data given at 18°; interpolated for concentration.

[12] Krchma, B. S., *Thesis,* **1927,** University of Wisconsin. Measurements made at 23°.

the two sets of data is not particularly good is evident from the table. It may be said, however, that the difference between the values for pure water and those of the sugar solutions of each investigator are more significant than the actual numerical values of the dielectric constants and it is the differences which are of greatest importance for the data of this article. The dielectric constant data of Fürth[13] for aqueous sugar solutions do not compare favorably with those of Kockel and Harrington. The recent data of Walden and Werner[14] are limited to very dilute solutions of sugar; therefore they cannot be utilized here.

It is at once evident from these tables that the agreement between the actual change produced in the slope by the change of solvent and that required by the Debye and Huckel theory, using the best available dielectric constant data, is all that could be expected. The agreement is perhaps better in the case of the solubility relations of the salt of higher valence type because the actual change in slope produced is three times that in the case of the salt of simple valence type, making possible a more accurate determination of the percentage change in slope. The conclusion that the theoretical equation applies also for a mixed solvent is of particular interest.

Summary

1. Experimental data to test the validity of the Debye and Hückel theory with respect to the effect of a variation of the dielectric constant up to 15% have been presented. These data involve determinations of the change produced in the solubility of two complex cobalt ammine salts of different valence types, using the same solvent salt, but varying the solvent by the addition of sugar or ether to the water.

2. The validity of the limiting law with respect to a 15% variation of the dielectric constant, making due allowances for the accuracy with which the experimental slopes can be determined and the paucity of the dielectric constant data, is completely confirmed.

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[13] Fürth, *Ann. Physik*, **70**, 63 (1923).

[14] Walden and Werner, *Z. physik. Chem.*, **129**, 405 (1927).

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 173]

THE REGION OF EXISTENCE OF UNIMOLECULAR REACTIONS

BY LOUIS STEVENSON KASSEL[1]

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Rice and Ramsperger[2] and the author[3] have developed theories of unimolecular reactions based upon the assumptions of activated states, produced by collisions, and having specific reaction rates which are functions of their energy contents. If the rate of production of activated molecules is large compared to the rate of reaction, the fraction of the molecules present in the activated states will be very little affected by the reaction, and thus a first order reaction can be supported by a bimolecular activation process. But if the pressure is sufficiently decreased, a point will be reached at which the rate of production of activated molecules is no longer large compared to their rate of reaction, and the calculated first order constant for the reaction will begin to decrease, until eventually it will become proportional to the pressure and the reaction will have become of the second order.

Interpreted in terms of the collisions and the free paths occurring in the gas, this means that at high pressures in unimolecular reactions, where the mean free path is short, the time between an activating collision and a deactivating collision is seldom sufficient for the activated molecule to decompose; hence, when the pressure is decreased slightly, the rate of production of activated molecules is decreased, but the mean life of an activated molecule is increased in the same ratio, since this life is determined almost solely by the mean free path. Now at some pressure very much lower the mean free path will have become very long and most of the molecules which are activated will decompose before they suffer a collision. A decrease in the pressure will decrease the rate of production of activated molecules but it will have a very small effect on their average life, since this is determined chiefly by their specific reaction rates; and it will not increase very much the fraction of the activated molecules which decompose, since this fraction is already close to unity. Therefore the calculated unimolecular constant will decrease with the pressure and the reaction will no longer be first order. In the limit, when the time between collisions is so great that all of the activated molecules decompose, the reaction will, of course, be second order. The early stages of this transition have been observed by Hinshelwood and his students in the decomposition of propionaldehyde,[4] diethyl ether[5] and dimethyl

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[1] National Research Fellow in Chemistry.

[2] Rice and Ramsperger, THIS JOURNAL, **49,** 1617 (1927); **50,** 617 (1928).

[3] Kassel, *J. Phys. Chem.*, *32,* 225 (1928) and article in press.

[4] Hinshelwood and Thompson, *Proc. Roy. Soc. (London)*, **113A,** 221 (1926).

[5] Hinshelwood, *ibid.*, **114A,** 84 (1927).

ether? Ramsperger[7] has observed a somewhat larger portion of the change from first to second order in the decomposition of azomethane, and his results are in satisfactory agreement with the quantitative theories of Rice and Ramsperger and of the author.[3] The results obtained by Hinshelwood can also be explained by these theories but the test imposed here is not as severe as with azomethane. Nitrogen pentoxide does not exhibit a decrease in rate down to a pressure of at least 0.003 cm.[8] and it has not yet been possible to give a completely satisfactory explanation of this behavior. Ramsperger[9] has shown that azoisopropane does not decrease in rate down to a pressure of 0.025 cm.; at this same pressure, the rate of decomposition of azomethane has decreased to from 10 to 20% of its high pressure value, depending upon the temperature. Here, however, the results are in complete agreement with the author's theory. It had proved possible on the basis of this theory to account quantitatively for the results found with azomethane by assuming that of the 24 vibrational degrees of freedom of the molecule, six (one for each hydrogen atom) were of such high frequency that they were essentially frozen-in, and that the other eighteen had frequencies corresponding to 13.57μ. The value used for the diameter for collisional deactivation was 3.16×10^{-8} cm. If it is assumed that of the 60 vibrational degrees of freedom of azoisopropane, 14 (corresponding to the 14 hydrogen atoms) are essentially frozen-in, that the other 46 have the same frequency as in azomethane, and that the diameter is 4.47×10^{-8}, the rate will be about 95% maintained at 0.025 cm. and 300°, a temperature slightly greater than any Ramsperger used. This is almost certainly indistinguishable experimentally from complete maintenance, but there would be no difficulty in accounting for more than 95% by increasing the diameter slightly or decreasing the frequency assumed. Presumably, at still lower pressures, the reaction rate would begin to decrease noticeably.

Thus it appears that the theoretical prediction that at low pressures unimolecular reaction rates will decrease is borne out by most of the experimental data, and we may feel confident that the theory of these reactions is essentially correct. The theory of bimolecular reactions which is most generally accepted is that the energy of activation is supplied by the collision, and that the reaction occurs immediately. For these reactions it is an experimental fact that, within a factor of 2 or 3, we have

$$\text{number of molecules reacting} = \text{number entering into collision} \times e^{-E_0/RT}$$

This is frequently interpreted as meaning that when the available energy of the collision is at least E_0, both molecules will react. The author pre-

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[6] Hinshelwood and Askey, *Proc.* Roy. *Soc. (London)*, **115A,** 215 (1927).

[7] Ramsperger, THIS JOURNAL, 49, 912, 1495 (1927).

[8] Hibben, *Proc. Nat. Acad. Sci.,* 13, 626 (1927).

[9] Ramsperger, *ibid.,* 13, 849 (1927).

fers in some cases to regard it as an expression of the fact that the condition for reaction is the acquisition of the energy E_0 by a single bond in the molecule. For, whether the molecule is composed of two atoms or of more than two, the chance that in a collision, selected at random, the particular bond will acquire energy E_0 is $e^{-E_0/RT}$. It would thus seem as if every decomposition should have a bimolecular part, since this mechanism should be operative in the decomposition of azomethane as well as in that of nitrous oxide. Hence the typical decomposition of a polyatomic molecule will be bimolecular at high pressures, with a unimolecular part which is negligible; as the pressure is lowered the unimolecular part will gain in importance, and finally will dominate and then obscure the bimolecular part; as the pressure is still further decreased the rate of this unimolecular part will begin to decrease, until it will finally degrade from a first order reaction to a second order one. The constant for this low pressure second order reaction will, however, be greater than for the high pressure one, and may in the case of complex molecules exceed it by a factor of millions. The values of this constant should in general be sufficient data upon which to classify a second order reaction as the high or low pressure type, in the absence of other information. It is not to be expected that this entire sequence will fall within the range of realizable pressures for every reaction; for some substances the high pressure second order rate will be unobtainable, for others the low pressure one; for simple molecules, especially triatomic ones, even the first order phase may not be reached, and it is possible that in some cases the two second order rates will succeed each other too closely to permit the existence of an interval in which the reaction follows closely a first order law. In the special case of diatomic substances it seems reasonable to suppose that only the high pressure second order rate will exist, and that the reaction will therefore be bimolecular over the entire range of pressures. All of these considerations are to a large extent independent of the detailed theories which have been advanced by Rice and Ramsperger and by the author.[2,3]

It has just been shown that there are theoretical reasons for expecting unimolecular reactions to have a bimolecular part which is dominant at high pressures. This part has hitherto escaped experimental detection and it therefore becomes necessary to calculate the actual bimolecular rates which might be expected. The following list gives all of the unimolecular reactions which are generally accepted, and approximate expressions for their rates.

Acetone[10]	$\ln K = 34.95 - 68{,}500/RT$
Propionaldehyde[4]	$\ln K = 27.93 - 54{,}000/RT$
Diethyl ether[5]	$\ln K = 26.47 - 53{,}000/RT$
Dimethyl ether[8]	$\ln K = 30.36 - 58{,}500/RT$

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[10] Hinshelwood and Hutchinson, *Proc.* Roy. *Soc.* (London), 111A, 245 (1926).

Pinene[11]	$\text{in } K = 33.21 - 43{,}710/RT$
Azomethane[7]	$\ln K = 36.73 - 51{,}200/RT$
Azo*iso*propane[9]	$\text{In } K = 31.36 - 40{,}900/RT$
Nitrogen pentoxide[12]	$\ln K = 31.45 - 24{,}700/RT$

It is very easy to see by a short calculation that except for diethyl ether and propionaldehyde the bimolecular mechanism suggested could not contribute appreciably to the total rate; for the contribution to a first order constant would be

$$\text{In (contribution)} = \ln 4\sqrt{\frac{\pi RT}{M}}\,N\sigma^2 - E_0/RT$$

If we take $M = 25$, which is less than its actual value in any of the preceding reactions, T = 1000" K., which is greater than any actual value used, a = 10^{-7} cm., and N, the number of molecules per cc., as 2×10^{19}, which corresponds to a pressure of nearly an atmosphere even at room temperature, we find the contribution is given by

$$\text{In (contribution)} = 25.12 - E_0/RT$$

This is a greater contribution than is actually made in any of these reactions. If we repeat the calculation for diethyl ether, using the rather large molecular diameter a = 10^{-7} cm., we find that

$$\ln \text{(contribution)} = 23.61 - E_0/RT$$

This is only about $^1/_{17}$ of the observed unimolecular rate; this is at a pressure of one atmosphere, where the effect would be greater than in any actual experiment. Actually, the unimolecular constant is still increasing somewhat at 500 mm., beyond which the measurements have not been made, but it is impossible to tell whether this is due to the approach of the unimolecular part of the reaction to its full value, or to the bimolecular part. For all of the other reactions listed, the bimolecular part would be entirely inappreciable at pressures of an atmosphere or less.

In a diatomic molecule there is only one bond, and unless we admit the possibility of electronic activation all of the internal energy is stored in the same place. Hence it would seem that decomposition is constrained to occur at collision, and that the reaction must be quite exactly bimolecular. But if the molecule is triatomic or still more complex, the reaction should contain a unimolecular portion. Although there is no basis for making precise predictions, it would be expected that this unimolecular portion would be relatively less important in the simpler molecules, and in agreement with this it is found that the decompositions of such substances as nitrous oxide[13] and ozone[14] are definitely bimolecular. The

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[11] Smith, THIS JOURNAL, **49,** 43 *(1927).*

[12] Daniels and Johnston, *ibid.,* 43, 53 *(1921).*

[13] Hinshelwood and Burk, *Proc. Roy. Soc. (London),* **106A,** *284 (1924).*

[14] Warburg, *Ann. Physik,* 9, *1286* (1902); Clement, *ibid.,* 14, *341 (1904);* Perman and Greaves, *Proc.* Roy. *Soc. (London),* **80A,** *353 (1908);* Jahn, *Z. anorg. Chem., 48, 260 (1906);* Clarke and Chapman, *J.* Chem. *Soc.,* 93, *1638 (1908);* Chapman and Jones, *ibid.,* 97, *2463 (1910);* Wulf and Tolman, THIS JOURNAL, 49, *1183 (1927).*

most complex molecule known to the author to decompose according to a second order law is acetaldehyde.[15] If it is attempted to regard this reaction as being the low pressure phase of a unimolecular reaction, difficulties are encountered. Unless the frequencies of all the oscillators are made extremely high, the total number of oscillators must be kept very small, and the diameter of the molecule less than is usually necessary to make the reaction bimolecular at a pressure of one atmosphere. Then, to account for the results with propionaldehyde, where the reaction is unimolecular at high pressures, it is necessary to make unreasonably great increases either in the number of oscillators, the associated wave length or the molecular diameter. Even if this is done, there are two remaining difficulties; the first is that the effect of hydrogen in maintaining the unimolecular rate, which was found for propionaldehyde, just as for the ethers, is absent in the case of acetaldehyde;[16] the other is that the reaction is not quite bimolecular; the plot of the reciprocal of the "half-life" against the pressure gives a straight line, as it should, but this line does not pass through the origin; instead it has a positive intercept on the half-life axis.[17]

All of these difficulties are overcome by regarding the decomposition of acetaldehyde as being composed of a unimolecular contribution, produced by the same sort of mechanism as in the case of propionaldehyde, and a bimolecular contribution, produced by the immediate reaction of molecules at collisions, the latter being of greater importance at pressures above 100 mm. We may then write

$$-\frac{dn}{dt} = an^2 + bn$$

The integral of this is

$$t = \frac{1}{b}\ln\frac{(an + b)\, n_0}{(an_0 + b)\, n}$$

and hence the half-life is given by

$$t_{1/2} = \frac{1}{b}\ln\frac{an_0 + 2b}{an_0 + b}$$

When an_0 is large compared to b (that is, when the bimolecular contribution is dominant), this may be written

$$t_{1/2} = \frac{1}{b}\left[\frac{b}{an_0 + b} - \frac{1}{2}\left(\frac{b}{an_0 + b}\right)^2 + \dots\right] \cong \frac{1}{an_0 + b}$$

and hence

$$1/t_{1/2} \cong an_0 + b$$

It is found that the plot of $1/t_{1/2}$ against n_0 actually deviates but slightly from a straight line over its entire course. In the accompanying figure

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[15] Hinshelwood and Hutchison, *Proc. Roy. Soc. (London)*, **111A**, *380* (1926)

[16] Hinshelwood and Askey, *ibid.*, **116A**, *163* (1927).

[17] Hinshelwood and Hutchison, *ibid.*, **111A**, *382* (1926).

the points represent Hinshelwood and Hutchison's measurements at 518°, and the line is the calculated curve for **a** = **5.1** $\times 10^{-6}$, and **b** = 4.2×10^{-4}, the time being measured in seconds and the pressure in mm. This value for the bimolecular constant is only slightly less than that which Hinshelwood and Hutchison reported from their uncorrected measurements. If it is assumed that the unimolecular reaction has the same temperature coefficient (except for the omission of the factor $T^{1/2}$, which is proportional to the number of collisions) as the bimolecular reaction, then the unimolecular part is given by

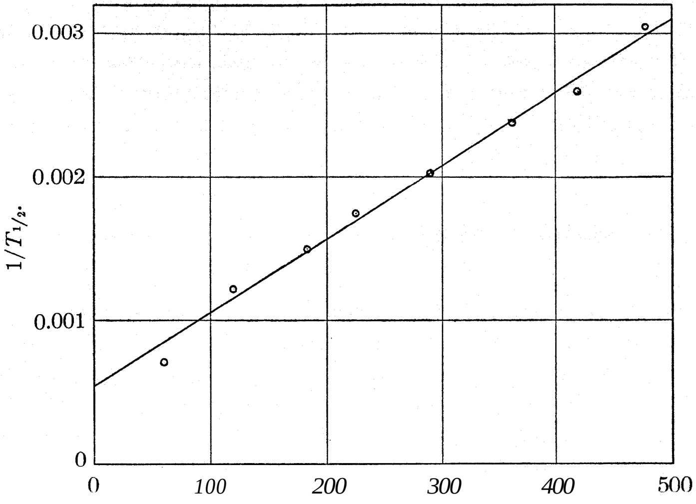

Fig. 1.

$$\ln K = 21.18 - 45500/RT$$

On the mechanism presented the temperature coefficients would be the same, but this cannot be regarded as certain in the absence of experimental evidence. For the two other cases in which pairs of similar substances have been studied (dimethyl ether–diethyl ether and azomethane–azo*iso*propane) the simpler molecule has given larger values of E_0 and of A, in $K = Ae^{-E_0/RT}$; here, when it is assumed that the two temperature coefficients are the same, E_0 and A for the unimolecular phase of the acetaldehyde decomposition are both less than for propionaldehyde. There is no reason apparent why this should not be the case, but the matter can only be settled by experiments over a range of pressures and temperatures.

If it is assumed that the unimolecular part of the decomposition is actually given by

$$\ln K = 21.18 - 45500/RT$$

it is possible to make calculations on the maintenance of this reaction rate, with various numbers of oscillators, of various frequencies. It is thus easy to show that down to pressures of about 50 mm. at least the rate would be maintained. It would be possible to account for maintenance at much lower pressures if the need arose.

It is not intended to imply that in all bimolecular reactions the reaction occurs entirely, or even chiefly, through collisions which cause one of the colliding molecules to dissociate; this process should always occur, but it may contribute very little to the total reaction rate in special cases; thus the heat of dissociation of hydrogen iodide is certainly greater than 60,000 cal., while the critical energy, calculated from the temperature coefficient of the decomposition, is but 44,000 cal. It thus seems likely that in this case the reaction which actually occurs at collision is

$$\mathrm{HI} + \mathrm{HI} = \mathrm{H_2} + \mathrm{I_2} \tag{1}$$

and that the parallel reaction

$$\mathrm{HI} + \mathrm{HI} = \mathrm{H} + \mathrm{I} + \mathrm{HI} \tag{2}$$

does not contribute much to the total rate. If the necessary condition for the first reaction is that the collision shall exceed a certain critical "violence," then the rate due to reaction (1) will be approximately $N_c e^{-44,000/RT}$, while that due to reaction (2) will be about $N_c e^{-60,000/RT}$, where N_c is the number of collisions. It is evident that the first rate would be extremely large compared to the second. Indeed, it may actually be found that with most simple chemical substances the dominant portion of the reaction is of the type (1). In fact, it has been recently suggested by Kornfeld[18] that the explanation of the tendency of simple substances to decompose according to bimolecular laws and of more complex molecules to exhibit unimolecular decompositions is to be found, not in the numerous degrees of freedom of the latter molecules, but in the fact that the critical energy in processes which produce free atoms is much greater than in those which do not, and that reactions of type (2) are thus handicapped.

In any actual gaseous decomposition all of these mechanisms and possibly others should be operative at the same time and it is in general impossible to predict which of them will be dominant under given conditions. On the other hand, when any single reaction has been studied over a great enough range of temperatures and pressures, it may be found possible to decide, with a considerable degree of certainty, what processes are chiefly responsible for the reaction. Thus, in the case of acetaldehyde, if it is found that the unimolecular reaction has the same temperature coefficient as the bimolecular one, it would seem reasonable to conclude that the dominant bimolecular process is of type (2), while if the unimolecular part of the reaction has a larger temperature coefficient, then the dominant

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[18] Kornfeld, *Z. physik. Chem.*, 131, 97 (1927).

bimolecular process must be of a different type, and (1) would be a reasonable guess. In no case, however, are any of these mechanisms to be considered as more than tentative hypotheses, since it is impossible to determine molecular processes from a study of the kinetics of a reaction.

The most important problem in the field of homogeneous gas reactions has been, not to unravel the precise mechanism of any single reaction, but to account for the order of magnitude of the rates of unimolecular reactions and to interpret both unimolecular and bimolecular reactions by means of a single, coherent scheme. Some few minor difficulties, chiefly associated with nitrogen pentoxide, still remain, but the method of solution of the problem has been indicated, and the solution itself, at least in its main features, has been given by the work of Lindemann, Christiansen, Hinshelwood, Rice, Ramsperger, and others.[3]

It may be pointed out that the table of reaction rates presented above is in disagreement with the formula first presented by Dushman[19]

$$K = \nu e^{-\frac{Nh\nu}{RT}}$$

In the following table the values of $\ln A$ calculated from this formula are compared with those found experimentally.

	$\ln A$ (calcd.)	$\ln A$ (obs.)		$\ln A$ (calcd.)	$\ln A$ (obs.)
Acetone	34.22	34.95	Pinene	33.77	33.21
Propionaldehyde	33.98	27.93	Azomethane	33.93	36.73
Diethyl ether	33.96	26.47	Azoisopropane	33.70	31.36
Dimethyl ether	34.06	30.36	Nitrogen pentoxide	33.20	31.45

The fair agreement obtained in the cases of acetone, pinene and nitrogen pentoxide loses any significance it might have had when the wide range of variation of the observed values is compared with the relatively constant computed values. Also, the statement made by Hinshelwood[10,5,6] that at temperatures at which E_0/RT is the same, all unimolecular reactions have about the same rates is seen to be only very roughly correct; for this is equivalent to saying that $\ln A$ is a constant for all reactions, while actually it is greater by 10 units for azomethane than it is for diethyl ether, corresponding to a difference in reaction rates at corresponding temperatures of more than 20,000-fold.

Summary

The typical homogeneous gaseous decomposition passes through three stages: at high pressures it is second order, due to reaction occurring at collisions; at lower pressures the rate becomes first order, the dominant factor being spontaneous decomposition of activated molecules, which are produced by collisions rapidly enough to maintain essentially the Maxwell-Boltzmann quota; at rather low pressures the reaction is again second order, though the rate constant is greater than for the high pressure stage;

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[19] Dushman, THIS JOURNAL, 43, 397 (1921).

in this stage of the reaction nearly all of the activated molecules decompose, since collisions, which could cause deactivation, have now become infrequent. The decomposition of acetaldehyde is an example of a reaction in the process of transition from the high pressure bimolecular stage to the unimolecular stage; the decomposition of azomethane indicates the transition from unimolecular to low pressure bimolecular.

There are several possible types of bimolecular reactions and in some cases it may be found possible to decide, by methods which have been indicated, to which of them any particular reaction belongs; of course, in general, all of the types proceed together, but one of them may account for all but a negligible fraction of the total reaction.

The formula for the velocity of unimolecular reactions proposed by Dushman is not in agreement with experimental data; indeed, the rates of these reactions have a much greater range of variation than is permitted by this formula.

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[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

SULFUR DIOXIDE AND ITS AQUEOUS SOLUTIONS. I. ANALYTICAL METHODS, VAPOR DENSITY AND VAPOR PRESSURE OF SULFUR DIOXIDE. VAPOR PRESSURE AND CONCENTRATIONS OF THE SOLUTIONS

BY CAROL E. MAASS AND O. MAASS

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The following is the first of two papers dealing with some of the physical properties of various phases of the two component system sulfur dioxide–water. The investigation had its beginning in an attempt to measure the conductivities of concentrated aqueous solutions of sulfur dioxide.

It was soon found, however, that other properties of sulfur dioxide had to be investigated before the conductivity could be measured. From some of the results obtained, these preliminary investigations proved to be of at least as great an interest as the main one and consequently the present paper is devoted solely to these. This work may be conveniently divided into the following topics: Purification of Suliur Dioxide, Analysis of Sulfurous Acid, Vapor Density Determinations, Vapor Pressures of Pure Sulfur Dioxide and its Aqueous Solutions, Concentrations in the Two Liquid Phase System, Sulfur Dioxide–Water.

A second paper, dealing with the conductivities and containing a theoretical discussion of the equilibria involved, will follow.

Purification of Sulfur Dioxide

It was found that particularly pure liquid sulfur dioxide could be obtained commercially. In order to test the gas for sulfur trioxide, it was passed into an acid solution of barium chloride, in which air-free water had been used, and from which the air was excluded. No precipitate was formed. The only impurity found in the sulfur dioxide was a small trace of water. The gas from the cylinder was therefore passed over phosphorus pentoxide tubes and condensed in tubes by a carbon dioxide–ether mixture. The liquid was then distilled a number of times in *vacuo*, the initial and final fractions being rejected. Cardoso[1] mentioned a yellowish liquid left as residue after some of his distillations. There was no sign of any such residue in the distillations carried out with the condensed product. The distillation was carried out in an all-glass apparatus. The pressure was controlled by means of a manometer. A tap leading from the purification apparatus was glass sealed alternately to the various pieces of apparatus (described in the following sections) where the experiments with the sulfur dioxide were to be carried out.

As a proof of the purity of the final fraction of sulfur dioxide, its vapor pressures were measured in the neighborhood of the boiling point and were found to agree exactly with the values obtained by Henning and Stock.[2] The vapor pressure determinations of these investigators were made with the greatest precision over the range −60 to −10°, and constituted one of the few physical constants of pure sulfur dioxide which was accurately known when this work was started.

Analysis of Sulfurous Acid

The estimation of sulfurous acid is described in most textbooks on quantitative analysis as being carried out very easily by means of a reaction with iodine which depends on the reducing power of sulfurous acid. It was soon found that in practice the titration of sulfurous acid by iodine was not so simple as the textbooks led one to believe. No constant results were obtained and two consecutive titrations of samples of the same sulfurous acid solution gave values differing by as much as 20%.

A search of the literature soon disclosed that others had met with similar results and various remedies had been suggested.[3] After considerable time had been spent in following some of the methods referred to above, a modification of them was worked out which gives accurate and reproducible results. This is true to such an extent that sulfur dioxide itself was used to calibrate the iodine solution.

A glass bulb B (Fig. 1) of 2–3 cc. capacity ending in a capillary tube bent in the manner shown was attached to a glass tube connected through tap A to the sulfur

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[1] Cardoso, *J. chim. phys.*, 23,829 (1926).

[2] Henning and Stock, *Z. Physik*, 4,226 (1921).

[3] (a) Bunsen, Ann. *chim. phys.*, [3] 41, 339 (1854); (b) Fordos and Gelis, *Compt. rend.*, 20, 771 (1845); (c) Finkner, "Quant. Analyse," 1871; (d) Volhard, Ann. *Chem. Pharm.*, 242, 94 (1873); (e) Macauley, J. *Chem. Soc.*, 121, 553 (1922); (f) Raschig, *Z. anorg. Chem.*, 17,577 (1904); (g) Hudson, J. *Chem. Soc.*, 127,1332 (1925).

dioxide purification apparatus and through tap D to a vacuum pump. After evacuation about 1 cc. of liquid sulfur dioxide was condensed in the bulb and the capillary sealed off with a hand blowpipe at the point marked C. The bulb was allowed to warm up to room temperature and then weighed. The bulb was then again cooled down by a carbon dioxide-ether mixture and the capillary broken off near the sealed end. By having a thin capillary but one whose walls were thick relative to its diameter and, furthermore, by using a new file to scratch the glass, no splintering occurred, so that the two broken parts represented the total weight of glass. The bulb is then allowed to warm up after the capillary is immersed in 50 cc. of a 2 N sodium hydroxide solution F, as shown in Fig. 1. The liquid sulfur dioxide which boils off is completely absorbed in the sodium hydroxide solution which then rises in the capillary as soon as all the liquid sulfur dioxide has evaporated. The moment this happens and before the liquid rises beyond a few centimeters the capillary is sealed off at E above the rising liquid. This bit of capillary is cleaned, dried out and, together with the sealed off bulb and piece of capillary first broken off, is carefully weighed. The difference in weight between this and the first mentioned weighing gives the weight of sulfur dioxide absorbed by the sodium hydroxide solution to an accuracy of 0.1 mg.

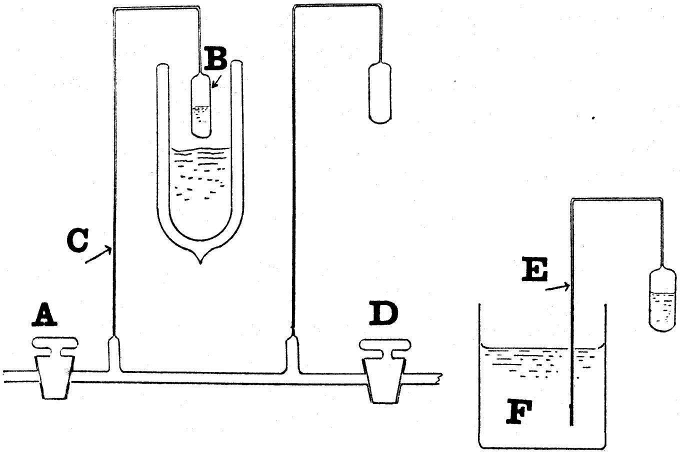

Fig. 1.

The essential feature governing the accuracy of the subsequent analysis was the solution of 0.1 g. of sugar in the 50 cc. of sodium hydroxide solution before the sulfur dioxide was absorbed. The 50 cc. was then made up to 250 cc. in a graduated flask, care being taken to wash all of the solution into the latter. This solution was then placed in a buret and 25 cc. of an iodine solution to be standardized was measured out from a pipet into an Erlenmeyer flask. This was diluted with an equal volume of water and 2 cc. of concentrated hydrochloric acid was added. The iodine solution was vigorously swished around in the Erlenmeyer flask and the sulfite solution was run in until the iodine color disappeared, a very sharp and final end-point being obtained. The above procedure can be used for any sulfurous acid solution by making the solution strongly alkaline, adding a small amount of sugar and then following the above directions.

The reasons for some of the steps in the procedure are explained by the following considerations. Only a strong alkalinity insures that no loss of sulfur dioxide takes place due to evaporation. Sulfite solutions oxidize in an inconsistent and most exasperating manner. Evidently the rate of oxidation is greatly increased by catalysts present in the form of small traces of impurities. In Ostwald's "Inorganic Chemistry,"[4] it is mentioned that the oxidation of sulfite is inhibited by the presence of a small amount of sugar, which Ostwald calls an anti catalyst. Of course, the probable action of the sugar is that it inhibits the action of the catalysts. The iodine solution is made strongly acid just before titration to neutralize the alkalinity of the sulfite solution.

As has already been indicated, at first no consistent results whatever could be obtained in the titrations even when the solutions were first treated with sodium bicarbonate. The method outlined above in the absence of sugar gave inconsistent results. This, as well as the importance of sugar for both uniformity and consistent results, is shown by Table I.

TABLE I

COMPARATIVE RESULTS IN SULFUROUS ACID ANALYSIS

Series	SO_2 dissolved in 250 cc., g.	Time after solution complete, min.	Sulfite soln. required per cc. of iodine soln., cc.	SO_2 per cc. of iodine soln., g.
A	0.9470	30	0.735	**0.002760 by first titration**
		50	.760	**.00604 by last**
		240	.900	
		2160	1.610	
B	1.022	30	.665	.002718
		50	.660	.002718
		240	.665	.002718
		2180	.665	.002718
C	1.095	30	.620	.002716
		50	.614	.002716
		2180	.620	.002716

The results A were obtained with a sulfite solution to which no sugar had been added. B and C illustrate the constancy of the sulfite solution in the presence of sugar and also the accuracy with which titrations can be repeated. It may be of interest to record the results obtained from an experiment in which this effect of sugar on oxidation was tested. Sulfur dioxide was passed into an acid solution of barium chloride, made up from water through which air had been passed. The solution was divided into two parts, one of which contained a trace of sugar. It was found that the oxidation of the sulfur dioxide, as indicated by the formation of the white precipitate of barium sulfate, proceeded very much more slowly in the beaker which contained the sugar.

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[4] Ostwald, "Grundlinien der Anorganische Chemie," 4th ed., Verlag T. Steinkopff, Dresden und Leipzig, 1919, p. 323.

Vapor Densities of Sulfur Dioxide

Reliable values for the vapor densities of sulfur dioxide were known only at 0°.[5] The work described in the following sections required an accurate knowledge of the vapor densities at other temperatures and therefore measurements were carried out over the range −6 to 32°.

The method employed was similar to that described by Maass and Russell.[6] The values for M, the apparent molecular weight, as obtained by this method are given in Table II.

TABLE II

VARIATION OF M WITH TEMPERATURE

T, °C.	p, cm.	M
34.05	75.33	65.20
22.9	75.93	65.27
10.35	75.50	65.42
1.4	75.54	65.60
0.8	75.59	65.61
− 6.55	75.53	65.76

From the graph the value for M at 0° is found to be 65.62 which gives the weight of one liter under standard conditions as $65.62/(0.08209 \times 273.1) = 2.927$ g. This agrees exactly with the figure obtained by previous investigators. As was mentioned above the zero degree value was the only one which had hitherto been determined accurately.

It may be of interest to show that the apparent molecular weight is the most convenient way of tabulating p, V, T data for a gas from the point of view of calculating the weight of any quantity of gas taken out of a given volume. Use is made of the fact that up to pressures of several atmospheres, the apparent molecular weight at a definite temperature varies in a linear way with the pressure[7] so that in the case of sulfur dioxide, whose theoretical molecular weight is 64.06, the apparent molecular weight at any pressure, p, is $[64.06 + (M-64.06)p]/76$. Hence the weight of gas contained in a volume, V, at pressure, p, and temperature T, °A., is

$$\{[64.06 + (M-64.06)\,p]/76\}\; Vp/RT\ 76$$

It follows (without going through the algebraic steps) that the amount of sulfur dioxide taken out between pressures p_1 and p_2 is given by

$$\frac{p_1 - p_2}{76}\left\{64.06 + \frac{M - 64.06}{76}(p_1 + p_2)\right\}\frac{V}{RT}$$

which is a more exact and general equation than that deduced by Maass

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[5] (a) Baumé, J. *chim. phys.*, 6, 1 (1908); (b) Jaquerod and Pintze, *Mém. Genève*, 35, 589 (1908); (c) Guye, *Chem.-Ztg.*, 36, 402 (1912); (d) Scherrer, *Sitz.* Akad. *Wien*, 123, IIA, 931 (1914).

[6] Maass and Russell, THIS JOURNAL, 40, 1847 (1918).

[7] Maass and Mennie, Proc. *Roy. Soc.* (London), 110A, 198 (1926).

and Boomer.[8] The above formula was used in all subsequent work, the values of M being read off from a graph,

Vapor Pressures of Pure Sulfur Dioxide and of its Aqueous Solutions

In the following section, measurements of the vapor pressures of pure sulfur dioxide and its aqueous solutions are described. The tables containing the results are grouped together at the end of the description of the experimental details. The results of other investigators follow so that comparisons may be made.

The apparatus which was devised for the measurement of vapor pressures is shown in Fig. 2. Tap B led to the sulfur dioxide purification apparatus and tap E to a vacuum pump. B was a flask separated from a small bulb L by a Morrison pressure tap C.[9] Another pressure tap D led to the bulb F containing the solution, stirred by a glass stirrer H in which an iron nail was sealed. This stirrer was operated by a solenoid I in series with an automatic current breaker.[10]

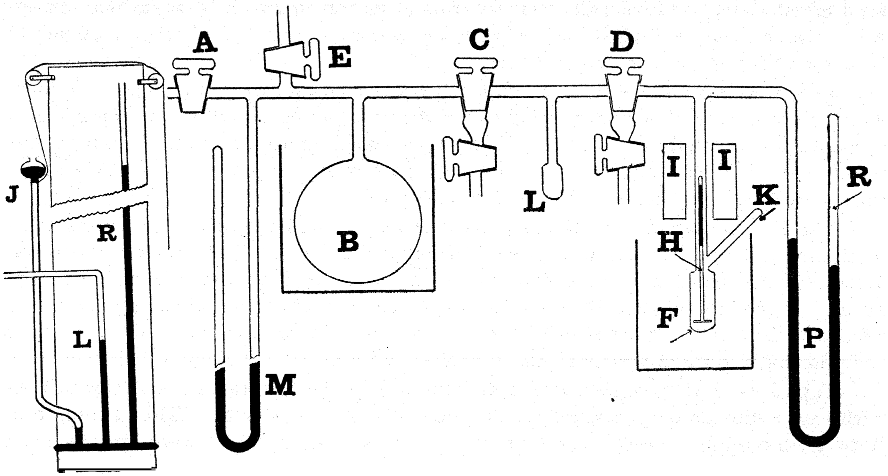

Fig. 2.

The usual form of manometer (M) served to measure the pressures in the apparatus from A to D and a pressure manometer P on which pressures up to twenty atmospheres could be read was employed to measure the vapor pressures of the solutions. The closed arm R of manometer P instead of being evacuated was filled with air at atmospheric pressure when the mercury was level in both arms of the manometer. Before the manometer was put together the volumes of R were carefully measured for various positions of the mercury in this arm and these results plotted on a graph. A glass mirror scale made it possible to read the mercury levels to 0.1 mm. and a thermometer placed beside R gave the temperature T, °C., of the enclosed air.

However, at the higher pressures, when solutions of water in sulfur dioxide were examined, this did not register pressure changes accurately enough. Hence another

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[8] Maass and Boomer, THIS JOURNAL, 44, 1727 (1922).

[9] Maass and Morrison, *ibid.*, 45, 1677 (1923).

[10] Maass, *Trans. Roy. Soc. (Canada)*, 11, 137 (1917).

type of manometer was constructed which was then also used in the redetermination of values found by means of the enclosed air manometer.

The manometer consisted of two arms, R and L, one of which was 4 meters long, fastened to a scale and attached to a wooden framework. A ladder placed a foot away, in front of the scale, made it possible to read the position of the mercury column at any height. The long arm of the manometer was open at the top so that atmospheric pressure had to be added to the pressure as read by the difference in level between the mercury columns in the two arms. Thermometers were placed at intervals along the mercury column so that the temperature of the latter could be reduced to 0°. J was a leveling bulb connected to the bottom of the manometer (shown in Fig. 2) by a thick, stout rubber tube. This leveling bulb was held by a rope which passed over a pulley at the top of the wooden framework. As the sulfur dioxide warmed up and the pressure in F rose, the leveling bulb was raised by means of the rope to keep the mercury in the short arm at a constant level.

When the sulfur dioxide in bulb F was at the temperature of carbon dioxide–ether, its pressure was only a few centimeters of mercury. This, combined with the fact that the long arm was open to the atmosphere, made it necessary for the short arm to be at least 80 cm. long to prevent the mercury from being forced into F by atmospheric pressure. Each time the bulb F was cooled down by carbon dioxide and ether, care had to be taken to lower the mercury.

The procedure followed in the vapor pressure measurements was then as follows. Through side arm K a known weight of water was placed in bulb F by means of a specially constructed weight pipet. K was then sealed off and the water frozen by surrounding bulb F with liquid air. All taps except A were then opened so that the apparatus could be completely evacuated through tap E.

Tap D was then closed and the water in F was allowed to melt. Any air occluded in the ice bubbled into the evacuated space above the water. The water was frozen again and the space once more evacuated. The freezing of the water expelled all the air and at the low pressure none of this redissolved, as could be shown by repeating the process, when no occluded bubbles could be observed in the ice. This process, then, ensured that the water was quite free from dissolved air.

Taps E and D were then closed and the rest of the apparatus filled (through A) with sulfur dioxide to a pressure p, as registered by manometer M. The volume from A to D, including tubing, flask B, bulb L, etc., was accurately known, having been previously determined. By means of a carbon dioxide–ether mixture a small amount of sulfur dioxide was condensed in bulb L and tap C closed. After the sulfur dioxide had been allowed to warm up to room temperature, the stirrer was started and tap D was opened so that the sulfur dioxide from bulb L distilled into the water. Tap D was then closed, tap C opened and the pressure p_2 read on the manometer. The amount of sulfur dioxide which had passed through D could therefore be calculated with great accuracy by means of the equation developed in the preceding section and by making use of the data given here.

The sulfur dioxide which had passed through tap D may be divided into two portions, that which enters into the water and the quite appreciable amount which fills the tubing above leading to manometer P. The pressure registered was practically all due to the partial vapor pressure of the sulfur dioxide, as the vapor pressure of water over the temperature range where experiments were carried out is relatively very small. The volume of bulb F and the tubing leading to the left arm of the manometer P was accurately known and hence the amount of sulfur dioxide above the liquid in bulb F could be calculated. Hence the concentration of the solution formed in bulb F could be evaluated with great precision.

A few words are now in place with regard to the function of the magnetic stirrer. Naturally it takes time for equilibrium to be established between a liquid and a gaseous phase. Indeed, it was found that without "a stirring" which both broke the surface of the liquid and circulated the gas above its surface true equilibrium was not established for several hours. As it was, even with the splendid stirring of the magnetic stirrer, which moved through the whole body of the liquid and right out of the surface in each stroke, it required five minutes for complete equilibrium to be established. Once this was established the vapor pressure registered had a definite value which remained unaltered. After reading the pressure for a given temperature and then altering the pressure by changing the temperature, it was found that on returning to the original temperature the original pressure was again registered exactly. The temperatures of the solutions were governed by a well stirred bath surrounding bulb F, the temperature being read by a Reichsanstalt thermometer. In some of the solutions a trace of sugar was added for reasons which are apparent from the section on analysis of sulfurous acid. It was found that a trace of sugar did not alter the pressures.

Again a sample calculation will be given in order that from the quantities involved the accuracy of the results may be judged. All pressures are given in cm. of mercury corrected to 0°. The weight of water placed in bulb I, as given by weight pipet and corrected to vacuum was 5.472 g.; initial pressure, p_1, 75.41; final pressure, p_2, 56.65; volume of flask B, bulb I, and tubing up to manometer, 0.3891 liter; temperature of gas, 25.8' ; apparent molecular weight of sulfur dioxide at 25.8°, 65.23; weight of sulfur dioxide

$$\frac{(75.41 - 56.65)}{76}\left\{64.06 + \frac{(65.23 - 64.06)}{76}(75.41 + 56.65)\right\}\frac{0.3891}{0.08209 \times 298.9} = 0.2587 \text{ g.}$$

Upward movement of manometer M during pressure change caused displacement of sulfur dioxide calculated from volume of tubing to be 0.0173 g.; weight of sulfur dioxide passing tap D, 0.276 g.; pressure registered by manometer P calculated to be 24.3 cm., giving 0.014 g. as the amount of sulfur dioxide above the solution when the volume of the tubing and the temperature were taken into account. Hence the percentage of sulfur dioxide in the solution is given by 0.262/(5.472 + 0.262) = 4.57%. The pressure of 24.3 cm. was registered when the solution was kept at 10°.

In this way the values of the vapor pressures of solutions at various concentrations and pressures were measured. When the solution of sulfur dioxide in water reached a certain concentration, a second liquid phase separated out, the solution of water in sulfur dioxide. The pressure registered by this two-phase system is, of course, independent of the relative amounts of water and sulfur dioxide present. Its pressures were measured over a temperature range, 10–27°. The vapor pressures of pure sulfur dioxide were also determined over the same temperature range. For this, bulb F was first carefully dried in *vacuo* and then filled with pure sulfur dioxide.

TABLE III

TOTAL VAPOR PRESSURES OF SULFUR DIOXIDE SOLUTIONS AT DIFFERENT TEMPERATURES AND CONCENTRATIONS

T, °C.	Concn., %	Press., cm. of Hg at 0°	T, °C.	Concn., %	Press., cm. of Hg at 0°
10 0	4 57	24.3	22 0	4.40	37.8
	8.19	45 2		7.88	69.3
	11.64	67.4		11.17	102.2
	14.75	87.4		14.04	132.6
	18.91	124.5		18.22	178.3
	19.86	128.8	22 0	19.14	186.1
	23.10	154.3		22.32	222.2
16 5	4.48	31.0	25 0	6.9	66.2
	8.03	57.2		22.4	246.9
	11.42	84.4	27 0	4 32	44.8
	14.31	111.4		7 71	81.0
	18.57	151.9		10.95	118.3
	19.52	156.0		13.74	152.8
	22.71	188 4		17.85	206.9
				21.86	255.6

TABLE IV

VAPOR PRESSURES OF TWO PHASE SYSTEM SULFUR DIOXIDE–WATER

T, °C.	Press., cm. of Hg at 0°	T, °C.	Press., cm. of Hg at 0°	T, °C.	Press., cm. of Hg at 0°
10.0	166.6	22.7	258.9	16.0	204.4
11.3	175.2	25.0	277.4	18.0	219.6
16.5	209.8	27.0	297.3	19 9	234 8
22.0	254.1	11.0	172.2		

TABLE V

VAPOR PRESSURES OF PURE SULFUR DIOXIDE

T, °C.	Press., cm. of Hg at 0°	T, °C.	Press., cm. of Hg at 0°	T, °C.	Press., cm. of Hg at 0°
1.3	123.5	22.0	264.1	15.0	207.0
2.26	127.6	27.0	314.2	18.0	230.5
10.0	173.3	0.2	117.27	22.6	269.8
16.5	218.8	9.1	168.17		

In Fig. 3 the values of the vapor pressures contained in Table III are plotted against concentration. The determinations carried out at the same temperature are connected by lines, which show that the pressures increase more gradually with concentration, to become finally nearly linear, at the higher concentrations. The values in Table IV are plotted as horizontal lines, being independent of the concentration. Fig. 4 shows the relation of vapor pressure to temperature of pure sulfur dioxide (Curve I) and the two liquid phase system (Curve II). The curves in this figure were drawn from the points marked with circles, which were determined by the open-end manometer. The values found by the enclosed air manometer are marked in by crosses. It will be seen that in the case of the pure sulfur dioxide these crosses lie on the curve. In Curve II the crosses lie slightly above the curve.

Vapor pressures of aqueous solutions of sulfur dioxide have been determined by Schoenfeld,[11] Sims[12] and Hudson.[3g] By recalculation and extrapolation, the results of the two latter investigators at low concentrations are found to be in good agreement with those of the authors, although the experimental methods employed were quite different. In the present work a larger range of concentration and pressure was covered and the temperature range, 10–27°, was more fully investigated.

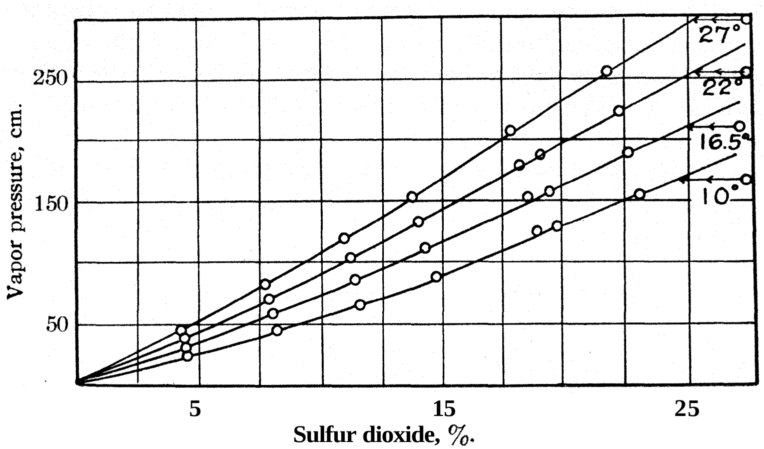

Fig. 3.—Variation of vapor pressure with concentration of sulfurous acid solutions at four different temperatures.

With regard to the vapor pressure of pure sulfur dioxide, the authors' value at 0° is in agreement with that obtained by Cardoso[13] and Regnault.[14] At higher temperatures Cardoso's values differ in an irregular way from those obtained in the work described.

Roozeboom[15] measured a few pressures of the hydrate $SO_2 \cdot 7H_2O$, when in equilibrium with the liquid phase. He found that the vapor pressure of this hydrate at the quadruple point, 12.1°, was 177.3 cm. This should correspond to the vapor pressure of the two liquid phase system at 12.1°. The curve in Fig. 6 gives a slightly higher value, 179.0 cm.

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[11] (a) Schoenfeld, Ann., 95, 1 (1855); (b) Landolt-Börnstein, Tables, 5th ed., 1923, p. 762.

[12] Sims, Trans. *Chem. Soc.*, 14, 1 (1862).

[13] Ref. 1, p. 835.

[14] Regnault, "Relation des Experiences," II, p. 581.

[15] Roozeboom, *Z. physik.* Chem., 1,206 (1887).

Concentrations in the Two Liquid Phase System Sulfur Dioxide–Water

The vapor pressures contained in Tables III and V can be used in connection with the determination of the solubility of sulfur dioxide in the water phase of the two liquid phase system. This is made plain by a consideration of the curves in Fig. 3. As sulfur dioxide is added to the water, the solution becomes increasingly stronger and the pressure correspondingly higher. When the water phase reaches its saturation concentration, a second liquid phase separates out—a solution of water in sulfur dioxide. Further addition of sulfur dioxide results in a readjustment of the relative amounts of the two phases to a new equilibrium but the percentage composition of both phases remains unaltered. That is, the percentage composition of the water phase does not change after its saturation concentration has been reached, and its pressure therefore remains constant. The constant pressure corresponds to the horizontal line of the graph. The percentage corresponding to the point where this line cuts the extrapolated pressure concentration curve gives the solubility of sulfur dioxide at that temperature.

This is a sensitive and novel method of estimating the concentrations of the aqueous liquid phases. In Table VI these values (probably correct to 0.1%) are given.

TABLE VI

TEMPERATURE VARIATION OF CONCENTRATION IN THE AQUEOUS PHASE

T, °C.	10.0	16.5	22.0	27.0
SO_2 in aqueous phase, %	24.60	24.92	25.24	25.20

The concentrations of the aqueous phases are definitely known. However, the value at 12.1° is only 24.7% of SO_2, notably different from the concentration of the liquid phase at the quadruple point as measured by Roozeboom, namely, 31%.[15] It was therefore deemed advisable to check one of the concentrations by direct analysis.

On account of the high vapor pressure of the system after true equilibrium has been established, it is a matter of great difficulty to remove one of the liquid phases without upsetting this equilibrium. This is a general experimental problem met with in the examination of systems of this type, for instance in the system H_2O–Cl_2. The solving of this problem as described below is therefore of some importance.

In Fig. 5 tap A leads to the sulfur dioxide purification apparatus and tap E to a vacuum pump. A tube B is connected to the system by a glass tube with a constriction. A side tube C on B leads through a capillary D to a smaller tube F of about 2 cc. capacity, the top of which ends in a closed capillary, H. Ten cc. of water had been placed in B before it was sealed on. This water was frozen and the apparatus evacuated through E. Approximately 10 g. of sulfur dioxide was then condensed on top of the ice in B and B sealed off at the constriction. It was then placed in a water-bath and allowed to warm up to the desired temperature. The liquid layers which formed in the bottom of B were well shaken up, care being taken that no liquid entered C. The tube was allowed to stand at constant temperature until the two layers were quite separate and then the tube was carefully tilted until some of the liquid in the upper layer ran into C, filling it with some 4 cc. of liquid which was held in place by the sulfur dioxide vapor in F. The tube B was then tilted back into a position as indicated in the second part of the diagram (Fig. 5). On gradually immersing F in a cooling bath the contraction of the sulfur dioxide vapor in E caused some of the liquid in C to flow through the capillary. Before all the liquid from C had entered F, F was plunged quickly into a carbon dioxide-ether mixture so that the liquid flowing through the capillary was frozen. This was the essential feature of the whole method because the liquid in F was trapped and represented the true equilibrium condition corresponding to the temperature of the water-bath. The bottom of tube B was then immersed in a second carbon dioxide–ether bath. the tube F still being kept in the first one. All the liquid remaining in tube C above the frozen part in the capillary distilled back into C. The capillary was then sealed off at

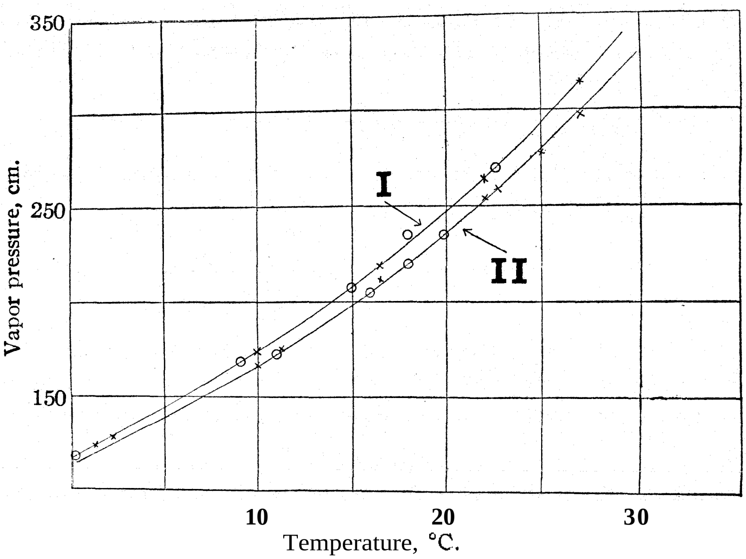

Fig. 4.—Variation of vapor pressure with temperature. I. Sulfur dioxide. **11.** The two phase system sulfur dioxide-water.

K. Tube F was allowed to warm up, weighed, cooled again in a carbon dioxide-ether mixture and the capillary tubes were broken off. The ends of the capillaries were then placed beneath the surface of a sodium hydroxide sugar solution and the contents of F allowed to warm up and dissolve. The glass was washed, dried and weighed.

The analysis of the solution was carried out as described in a former section. A sample calculation is given below.

Temperature of water-bath, 20°

Weight of solution trapped in F, **1.525** g.

Solution in NaOH made up to 250 cc.

One cc. of iodine, equivalent to **0.002717** g. of SO_2, was found to oxidize 1.720 cc. of the solution in NaOH

Total SO_2 was, therefore, **0.2951** g.

SO_2 vapor trapped in F, **0.0121** g.

SO_2 in aqueous phase, **25.10%**

Three other determinations carried out at the same temperature gave practically identical values, thus confirming the results given in Table IV to within 0.1% SO_2.

An approximate estimate of the water in the sulfur dioxide phase of the two phase system can be derived by means of the vapor pressure curves shown in Pig. 4. In the two liquid phase system, the vapor pressure can he regarded as due either to the water or to the sulfur dioxide phase, since these phases are in equilibrium. If the pressure is regarded as exerted by the sulfur dioxide phase, it follows from the proximity of the two curves that the vapor pressure of pure sulfur dioxide is only slightly lowered by the dissolved water and that this can only be present in small amount in this phase. Since the solution is only a dilute one, calculations can be made by means of Raoult's law to deduce the amount of water dissolved.

This can be written

$$\frac{m}{M_{H_2O}} \times \frac{M_{SO_2}}{W} = \ln \frac{p}{p^1}$$

where m and W are the weights of the water and sulfur dioxide, respectively. Hence

$$\% \ H_2O = \frac{m}{W + m} = \frac{\frac{18}{64} 2.3 \lg \frac{p}{p^1}}{1 + \left(\frac{18}{64} 2.3 \lg \frac{p}{p^1}\right)}$$

This equation is based on the assumption that water is not associated when dissolved in liquid sulfur dioxide. The percentages calculated in this way must, therefore, represent the minimum possible water concentration.

TABLE VII

PERCENTAGE OF WATER IN SULFUR DIOXIDE PHASE OF TWO LIQUID PHASE SYSTEM, CALCULATED FROM VAPOR PRESSURE DATA OP FIG. 6

T, °C.	Vapor press. of pure SO_2, cm. of Hg at 0°	Vapor press. of two phase system, cm. of Hg at 0°	Water in soln., %
5.0	143.4	138.2	1.02
10.0	173.9	165.7	1.33
18.0	230.5	219.6	1.34
22.0	264.3	251.8	1.34
25.0	292.2	277.5	1.42
27.0	314.2	297.2	1.52

Since the above values had been obtained only by calculation, some direct experimental method of determining them was sought. The method employed was again based on the measurement of the vapor pressures, this time of solutions of water in sulfur dioxide. Due to the slight solubility of water in liquid sulfur dioxide, the difficulty in this procedure lay in making up solutions of known concentrations. The following device was finally used. A piece of ordinary glass tubing was drawn out into a capillary, at the end of which a small, thin walled bulb of about 3 mm.

diameter was blown. The bulb and tubing were then accurately weighed. Water was introduced into the bulb through the capillary by alternately heating and cooling the former, thus driving the air out of it. In this way enough water to fill the bulb (about 50 mg.) entered, and the capillary was then sealed off as close above the surface of water as possible. The piece of tubing was carefully dried and again weighed with the filled bulb. Thus the weight of water was definitely known. The little bulb was placed in tube F (see Pig. 2) through side arm K. The magnetic stirrer was kept down while the small bulb slipped past it down to the bottom of F. Side arm K was sealed off, tube P evacuated and surrounded with carbon dioxide–ether mixture. When the water was frozen, the bulb was broken by means of the magnetic stirrer, which acted as a hammer. The freezing of the water was important, as was found by experience. If the water bulb is broken in the evacuated space, the water will spatter all over the tube and evaporate into the space. After the bulb was broken, measured quantities of sulfur dioxide were added to the tube and the resulting pressures measured at 18°.

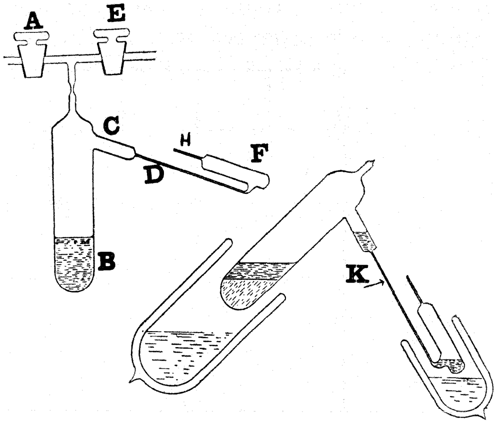

Fig. 5.

From the values contained in Table VII it was known that the saturation concentration of the water in sulfur dioxide would be small, in the neighborhood of 1 or 2%. The percentage of the solution calculated after the first addition of sulfur dioxide was about 5% of H_2O. This, of course, did not exist, and the amount of water left over, above the amount required to form a saturated solution of water in the sulfur dioxide, separated out to form a small amount of second phase, a solution of sulfur dioxide in water. The pressure registered at this point, then, was that due to the two liquid phase system at that temperature and agreed with the value found for this in Fig. 4.

As further quantities of sulfur dioxide are added, the pressure remains constant until a point is finally reached at which the amount of sulfur dioxide present is just sufficient to give the saturated solution of water. The second phase disappears and the pressure registered is due only to this saturated solution. Further addition of more sulfur dioxide raises the pressure until it nearly reaches the pressure of pure sulfur dioxide. This value is never quite reached, however, as no matter how much sulfur dioxide is present the original amount of water remains. The values obtained are given in Table VIII.

TABLE VIII

VAPOR PRESSURES FOR TWO PHASE SYSTEM, WATER–SULFUR DIOXIDE

Temp., °C.	H_2O in SO_2, %	Press., cm. of Hg at 0°
18	4.23	219.6
	2.16	219.7
	1.096	221.7
	0.735	224.9
	.494	226.8

These results are shown graphically in Fig. 6. At 18° the vapor pressure of pure sulfur dioxide was found to be 230.5 cm. and that of the two liquid phase system was found to be 219.6 (see Fig. 4). It will be seen from the figure that the last three values are almost in a straight line which, when produced in one direction, meets the zero percentage of water, that is, pure sulfur dioxide, at 230.5 cm. and cuts the **219.6** cm. isobar at 1.33% of water; 1.33% must, therefore, be the percentage of water dissolved in the liquid sulfur dioxide, that is, the saturated solution.

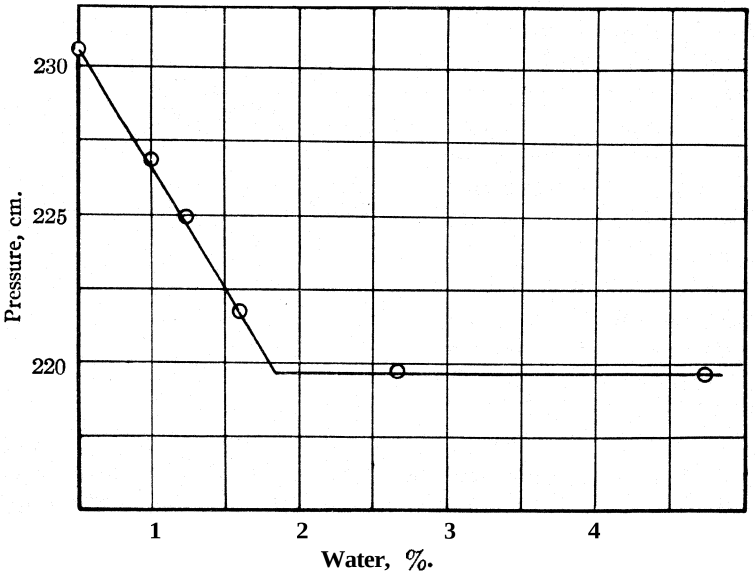

Fig. 6.

The value calculated from Raoult's equation is based on the assumption of unassociated molecules; this is justified by the experimental results. The agreement of **1.34%** calculated from the equation, with **1.33%** found experimentally, is better than the accuracy of the measurements.

Further measurements of the pressures of a 0.49% H_2O solution were made over a temperature range. Table IX contains the results obtained.

TABLE IX

TEMPERATURE VARIATION OF VAPOR PRESSURE OF A 0.49% H_2O SOLUTION

Temp., °C.	3.0	7.0	11.0	18.0	20.0
Vapor pressure, cm. of Hg at 0°	130.2	151.5	175.9	226.9	243.7

In the measurements just given, the concentration was so low that the pressure differences of solvent and solution were small and the error correspondingly large. Using the pressures in Table IX in Raoult's equation to determine the percentage, a mean value of 0.51% was given, which agrees remarkably well with the value 0.49%.

It is seen that the saturation solubilities of sulfur dioxide in water, and water in sulfur dioxide, do not vary appreciably with the temperature, namely, about 1% per 30° in the case of the former and 1% in 40° in the case of the latter. It will be interesting to determine the rest of the solubility curves for the higher temperatures. It is probable that complete mutual solubility will not occur before a temperature is reached not far removed from the critical temperature of sulfur dioxide, 155°.

Water is a substance which has a great tendency to associate. It does not do so in substances of similar nature. In these cases, however, there is far greater solubility than is shown by water in sulfur dioxide. Hence it is more probable that the water in the solution is combined with the sulfur dioxide to form sulfurous acid. The results obtained by Raoult's Law would be the same, within experimental accuracy, whether the water is present as unassociated water or as sulfurous acid. These are the only two possible conditions of the water and, from what has been said above, the existence of the water as sulfurous acid is the more probable.

Acknowledgment is made to the Research Council of Canada for a Bursary and Studentship awarded to one of us during the period in which this work was carried out.

Summary

A procedure for accurately analyzing solutions of sulfurous acid is described.

The apparent molecular weights of sulfur dioxide were measured over the temperature range—5 to 35°. An equation is developed in terms of apparent molecular weight which gives the most convenient and accurate evaluation of the weight of any gas taken out of a known volume when the initial and final pressures are measured.

A convenient method for measuring vapor pressures of solutions containing one volatile component is described. The vapor pressures of aqueous solutions of sulfur dioxide were measured over the temperature range 10–27°. All possible concentrations were covered. The vapor pressures of pure sulfur dioxide were measured over the range 1–27°. The vapor pressures of the two liquid phase system were measured over the range

10–27°. A comparison of values found by other investigators is included. It is shown that the concentration of the volatile component in the water, phase can be determined by means of the vapor pressure measurements and the concentration of water in the sulfur dioxide phase, approximately calculated by using Raoult's Law.

A method was designed for separating a portion of one liquid phase from any three phase system (liquid–liquid–gas) which is in equilibrium at pressures which are so great that there is difficulty in obtaining accurate analysis of the equilibrium concentration. This method was employed for measuring the concentration of sulfur dioxide in the aqueous phase and the values deduced from the vapor pressure measurements for the range 10–27° were confirmed at the temperature where measurements were made.

A method was devised by means of which the concentration of water in the sulfur dioxide phase can be more exactly determined. This method consisted in the measurement of vapor pressures of solutions of water in sulfur dioxide, and gave values agreeing very closely with those calculated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT.
III. THE TITRATION OF IODIDE

BY H. H. WILLARD AND PHILENA YOUNG[1]

RECEIVED MARCH 16, 1928 PUBLISHED MAY 5, 1928

Introduction

Previous work with ceric sulfate as a volumetric oxidizing agent2 suggested the importance of investigating potentiometrically the iodide-ceric salt reaction. Lange[3] stated that since ceric sulfate, even in the most dilute solutions, set free iodine from potassium iodide, it might be used as an oxidizing agent in volumetric analysis. Numerous investigators have made use of this reaction[4] as an iodimetric method for ceric cerium, their procedure being to treat the ceric salt with excess iodide in acid solution and to titrate the iodine liberated with thiosulfate. The direct titration of iodide with ceric sulfate, however, or the reverse reaction appears not

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[1] From a dissertation submitted by Philena Young to The Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Willard and Young, THIS JOURNAL, **50**, 1322, 1334 (1928).

[3] Lange, *J. prakt. Chem.*, 82,129 (1861).

[4] Bunsen, *Ann. Chem.*, 86, *285* (1853); Hartley, *J. Chem. Soc.*, *41*, 202 (1882); Browning, Hanford and Hall, *Z. anorg. Chem.*, 22, 297 (1899); Browning, *Am. J. Sci.*, 158,451 (1899); Power and Shedden, *J. Soc. Chem. Ind.*, *19,636* (1900); Meyer and Koss, *Ber.*, 35, 3740 (1902); Brauner, *Z. anorg. Chem.*, *34*, 207 (1903).

to have been worked out. The present paper describes the results obtained for these reactions in a hydrochloric or a sulfuric acid medium.

Experimental

The 0.05 N potassium iodide, prepared from especially pure material, was standardized against potassium permanganate[5] the normality of which had been determined with sodium oxalate. From two analyses the same factor, 0.05325 N, was obtained. The 0.1 *N* ceric sulfate was that prepared for earlier work[2] and was 0.5 *M* in sulfuric acid. It was standardized against sodium oxalate. Measured portions of potassium iodide were taken, diluted with water and sulfuric acid to definite volumes and titrated electrometrically with 0.1 *N* ceric sulfate. The results are shown in Table I.

TABLE I

TITRATION OF IODIDE WITH CERIC SULFATE IN SULFURIC ACID SOLUTION

KI, 0.05 *M*, cc	H_2SO_4 (sp. gr. 1.25) at beginning, cc	Vol. at beginning, cc.	KI, normality
25	0	100	0.05324
25	10	100	.05320
25	50	100	,05324
25	20	200	.05324
50	0	100	.05320
50	15	100	.05318
50	15	200	.05320

The potential break at the end-point amounted to 175–200 mv. per 0.03 cc. of 0.1 N ceric sulfate. In the presence of bromide the break was decreased. With a ratio of I : Br = 5 : 1, it became 45 mv. per 0.03 ce. of 0.1 N solution. The iodide factor obtained above corresponds to the reaction

$$2Ce(SO_4)_2 + 2KI = Ce_2(SO_4)_3 + K_2SO_4 + I_2$$

Thus, the titration of iodide in sulfuric acid solution with ceric sulfate or potassium permanganate, both of which have been standardized against the same primary standard, gives values which agree within less than 1 part in a thousand.

Measured portions of 0.1 N ceric sulfate were taken, diluted with water and sulfuric acid to 100 cc., and titrated electrometrically with 0.05 *M* potassium iodide. The results are shown in Table II.

TABLE II

TITRATION OF CERIC SULFATE WITH IODIDE IN SULFURIC ACID SOLUTION

$Ce(SO_4)_2$, 0.1 N, cc.	H_2SO_4 (sp. gr. 1.83) at beginning, cc.	KI, actual vol., cc.	KI, theoretical vol., cc.
25	5	25.40	25.36
25	10	25.38	25.36
15	5	15.24	15.22
50	5	50.75	50.72

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[5] Müller and Mollering, *Z. anorg. Chem.*, 141, 111 (1924), have shown that this titration is a very accurate one.

The potential break at the end-point amounted to 250–300 mv. per 0.03 cc. of 0.05 *M* iodide solution. The theoretical volumes were obtained by calculations from the data from two reverse titrations in which 25 cc. of potassium iodide required 24.66 and 24.64 cc. of ceric sulfate.

It was found possible to use this iodide titration after the bismuthate oxidation[6] of a cerous salt as a method for cerium. An approximately 0.05 N cerous sulfate solution was prepared from c. p. material. Pifty cc. portions of this solution, after oxidation with bismuthate and electrometric titration with ferrous sulfate which had been standardized electrometrically against standard ceric sulfate, were found from three analyses which agreed closely to contain 0.1745 g. of cerium. Table III gives the corresponding data for analyses in which the ceric sulfate formed was titrated with potassium iodide which had been standardized electrometrically against a ceric sulfate solution of known strength.

TABLE III

DETERMINATION OF CERIUM

$Ce_2(SO_4)_3$, 0.05 *N*, cc.	Ce found	Ce present
25	0.0873, 0.0874	0.0873
50	0.1745, 0.1748.0.1745	0.1745
100	0.3501, 0.3493, 0.3502	0.3490

Titration in Hydrochloric Acid Solution

Measured portions of 0.05 *M* potassium iodide were taken, diluted with water to a definite volume, treated with hydrochloric acid according to the procedures described below and titrated electrometrically with 0.1 N ceric sulfate, forming iodine chloride. The potassium iodide is the same solution as in Table I. Therefore its factor should be 2 × 0.05321 N or 0.1064 N, and was actually found to have this value by comparison with standard ceric sulfate. The results are given in Table IV.

TABLE IV

TITRATION OF IODIDE WITH CERIC SULFATE IN HYDROCHLORIC ACID SOLUTION

KI, 0.05 *M*, cc.	HCl (sp. gr. 1.18), cc.	Vol. at beginning, ec.	KI, normality
25	55	100	0.1060
25	45	100	.1060
25	35	100	.1061
25	25	100	.1062
25	45	300	.1060
15	45	100	.1058
50	45	100	.1057

Nearly all of the ceric sulfate was added rapidly to the iodide solution from a pipet before the hydrochloric acid was poured in. An odor of iodine was noticeable in the experiments and this loss was undoubtedly the cause

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[6] Metzger, THIS JOURNAL, 31,523 (1909).

for the slightly low results. If the acid was added before the ceric sulfate, the average factor obtained for the iodide was 0.1057–0.1058 *N*. When all but 0.2 cc. of the ceric sulfate, followed by the hydrochloric acid, was added to the iodide in a glass stoppered flask, the closed flask shaken thoroughly and its contents transferred to a beaker for the completion of the titration, the average factor from two closely agreeing titrations was 0.1061 N. Using a ratio of Br : I = 2 : 3, and 25 cc. of the iodide solution, the end-point break amounted to 30 mv. per 0.03 cc. of 0.1 *N* solution instead of 125–150 mv. for the same volume, the value obtained for the experiments in the table above. With 25 cc. of concd. hydrochloric acid per 100 cc., the equilibrium at the end-point was very slow; with less than this amount of acid, not practical.

Willard and Fenwick's[7] method of titrating iodide electrometrically in the presence of cyanide with permanganate, in which the iodide was changed quantitatively into iodine cyanide, was tested, using standard ceric sulfate instead of permanganate as the oxidizing agent. The reaction was found to be quantitative and the end-point equilibrium rapid.

A few experiments similar to those in Table IV were made using standard potassium iodate instead of ceric sulfate. The factor of the iodide varied from 0.1056 N to 0.1061 N as the conditions were changed, indicating the same loss of iodine.

Summary

1. Iodide may be determined very accurately in a sulfuric acid solution by electrometric titration to iodine with standard ceric sulfate. Moderate amounts of bromide may be present.

2. The titration of ceric sulfate with iodide in sulfuric acid solution goes smoothly and may be used in determining cerium after a bismuthate oxidation.

3. When iodide is titrated in a hydrochloric acid solution to iodine chloride with ceric sulfate, a small loss of iodine occurs during the oxidation and causes the results to be low—five parts or less in a thousand.

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[7] Willard and Fenwick, THIS JOURNAL, 45, 623 (1923).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. IV. THE DETERMINATION OF ARSENIC. V. THE DETERMINATION OF ANTIMONY

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Introduction

The action of cerium dioxide, either pure or impure, on arsenious acid in a hot sulfuric acid medium was investigated by Browning[2] who found that the oxide was only partially reduced, Job[3] in a paper on a method of induced oxidation of ceric carbonate stated that this compound did not oxidize potassium arsenite, but that in the presence of dextrose the latter was converted into arsenate. The direct titration of arsenious acid with a ceric salt, however, has not been tested, but such a reaction, if quantitative, would give another primary standard[4] with which to compare such oxidizing solutions.

Experimental

IV. THE DETERMINATION OF ARSENIC

A 0.1 N solution of sodium arsenite was prepared by dissolving pure arsenious oxide in sodium hydroxide, diluting and adding sulfuric acid until the solution was slightly acid, followed by 10 g. of potassium bicarbonate. The ceric sulfate solution was that prepared for earlier work[4] and was 1 M in sulfuric acid. Preliminary experiments showed that the direct titration of arsenious acid with ceric sulfate in hydrochloric acid solution at room temperature was impossible. The reaction was too slow. If the reaction was carried out at 75–85°, the equilibrium was rapid and the end-point break amounted to 100–130 mv. per 0.03 cc. of 0.1 *N* oxidizing agent. At 70° or below, or with less than 15 cc. of concd. hydrochloric acid per 100 cc. of solution, the equilibrium was too slow to be satisfactory.

Lang[5] found that chloride, bromide and iodide ions catalyzed the action between arsenious and permanganic acids in sulfuric acid solution, stating that this titration with permanganate went smoothly if 0.5 cc. of 0.005 *N* potassium bromide was added to the boiling hot arsenious acid solution containing at least 25% sulfuric acid. He attributed the action of the bromide to the following reactions

$$MnO_4^- + 5Br^- + 8H^+ = Mn^{++} + 5Br + 4H_2O$$
$$As^{+++} + 2Br = As^{+++++} + 2Br^-$$

Further work by this same author showed that the action of chloride alone as a catalyst was not satisfactory but that it served as a medium for the iodide catalysis at room temperature. Also, rather narrow experimental conditions had to be maintained when

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[1] From a dissertation submitted by Philena Young to The Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Browning, *Z. anorg. Chem.*, 22, 297 (1899).

[3] Job, *Compt. rend.*, 134, 1052 (1902).

[4] Willard and Young, THIS JOURNAL, 50, 1322 (1928).

[5] Lang, *Z. anorg. Chem.*, 152, 197 (1926).

bromide was the catalyst. Iodine, iodide or iodate proved to be the most satisfactory. If the titration were carried out in a warm sulfuric acid solution, the presence of iodide would introduce a positive error, that of iodate, no error. In a hydrochloric acid solution iodide would cause a positive error and iodate a negative one, as the final form of the catalyst in either case is iodine monochloride. The amount of these catalysts required was so small, however, never more than 1 drop of 0.005 *N* solution, that any error caused by their presence was negligible. An explanation of the catalytic action of iodine in any of these three forms in the above reaction is given in Lang's paper.

A similar catalytic action with these materials in the arsenious acid–ceric salt titration might be expected. Potassium bromide was the first substance tested.

A 0.1 *N* sodium arsenite, prepared as directed above, was diluted with water and the stated amount of hydrochloric acid, sp. gr. 1.18, to a volume of 100 cc. This solution, to which potassium bromide was added, was titrated electrometrically at the indicated temperature with approximately 0.1 *N* ceric sulfate. The results are shown in Table I.

TABLE I

CATALYTIC ACTION OF BROMIDE

$NaAsO_2$, 0.1 *N*, cc.	HCl, cc.	KBr, g.	Temp., °C.	$Ce(SO_4)_2$, 0.1 *N*, cc.	Rate of the reaction
10	25	1.25	25	9.55	Too slow to be practical
10	25	2.50	25	9.55	More rapid--only fairly satisfactory
10	25	5.00	25	9.56	Rapid—satisfactory
10	35	2.50	25	9.56	Rapid—satisfactory
10	35	5.00	25	9.55	Rapid—very satisfactory
10	50	1.25	25	9.52	Rapid—very satisfactory
10	50	0.00	25	9.57	*Very* slow--not practical
40	35	5.00	25	38.26	Very satisfactory
10	25	1.25	70–75	9.50	Rapid
10	25	0.50	70–75	9.52	Rapid
10	25	0.25	70–75	9.56	Rapid
10	25	0.12	70–75	9.58	Rapid
10	25	0.00	70–75	9.58	*Very* slow—not practical
10	15	0.25	70–75	9.57	Rapid
10	15	.50	70–75	9.55	Rapid
10	15	1.25	70–75	9.52	Rapid
10	35	0.12	70–75	9.58	Rapid
10	35	.50	70–75	9.53	Rapid
40	35	.25	70–75	38.30	Rapid
10	25	1.25	50–55	9.54	Quite rapid
10	25	2.50	50–55	9.53	Rapid
10	35	0.50	50–55	9.55	Rapid

The break at the end-point was 60–80 mv. per 0.03 cc. of 0.1 N ceric sulfate when the titration was made at room temperature and 100–150 mv. for temperatures of 50–75°. The data show that the amount of bromide necessary for a rapid reaction decreases as the temperature or the hydrochloric acid content is increased, but it is always much greater than that required to catalyze the arsenite–permanganate reaction. The quantity of arsenite may be varied through wide limits, and results were identical whether the ceric sulfate was added slowly or the greater portion of it rapidly from a pipet.

Ten cc. of 0.1 N sodium arsenite, a different solution from that used in the experiments in Table I, was taken and diluted with water, the stated amount of hydrochloric acid (sp. gr. 1.18) and catalyst to a volume of 100 cc. The titration was made electrometrically with approximately 0.1 *N* ceric sulfate at room temperature. The results are shown in Table II.

TABLE II

CATALYTIC ACTION OF IODINE OR IODINE CHLORIDE

HCl, cc.	Catalyst, cc.	$Ce(SO_4)_2$, 0.1 N, cc.	Actual blank, cc.	Theoretical blank, cc.	Rate of the reaction
35	5 g. KBr	10.18	....	....	A standardization
	KI, 0.0025 M				
30	1	10.25	+0.07	+0.05	Rather slow
30	2	10.30	+ .12	+ .10	Fairly rapid
30	5	10.47	+ .29	+ .25	Rapid
30	7	10.57	+ .39	+ .35	Rapid
30	10	10.72	+ .54	+ .50	Very rapid
30[a]	2	10.31	+ .13	+ .10	As rapid as preceding one
40	5	10.43	+ .25	+ .25	No more rapid than with 30 cc. of acid
	ICl, 0.005 M				
30	5	10.17	− .01	....	Rapid
30	2.5	10.17	− .01	....	Quite slow
30	15	10.16	− .02	....	Rapid
30	20	10.17	− .01	....	Rapid
30[b]	5	10.16	− .02	....	Rapid

[a] The temperature of the solution was 50–55° during the titration.

[b] Ten cc. of concd. sulfuric acid was added before the titration.

Titrations were not made with potassium iodate as catalyst, because obviously iodine chloride, causing no blank correction, is the most convenient catalyst. The break at the end-point amounted to 150–250 mv. per 0.03 cc. 0.1 *N* ceric sulfate.

The iodine chloride solution was prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 cc. of water and adding at once 250 cc. of concd. hydrochloric acid.[6] The solution thus obtained was 0.005 *M* in iodine chloride. It was adjusted electrometrically by adding dilute potassium iodide or iodate.

In a titration in which either iodide or iodine chloride is used as catalyst the solution is somewhat yellow. When near the end-point, the color becomes deeper, due to the presence of considerable iodine, and during the addition of the last 0.5 cc. of ceric salt the color slowly bleaches as iodine chloride is formed. At the end-point the solution is still a pale yellow when the conditions are such that equilibrium is reached rapidly, or a slightly deeper yellow if less favorable conditions have been used. In the former case it is possible, after some experience, to determine the end-point visually, as the slightest excess of ceric salt causes the solution

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[6] G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Company, New York, 1926, pp. 8, 9.

to become a deeper yellow again, but the method cannot be recommended as a sharp one.

A number of indicators were tested in the titration of arsenite with ceric sulfate in hydrochloric acid solution: methyl orange which is used in the arsenite–bromate reaction was not satisfactory, nor were indigo, diphenylamine or diphenylbenzidine. Methylene blue was the only indicator which appeared promising. A description of its use in the oxalate-ceric salt titration has been given[4] and the conditions for satisfactory results in the arsenite–ceric sulfate titration are the same: iodine chloride as catalyst, rapid equilibrium in the region of the end-point so that the yellow color bleaches quickly and addition of the indicator, 2 drops of 0.1% solution in water for each 100 cc. of solution, within 0.2–0.3 cc. of the end-point. In a series of experiments the amount of indicator was varied from 1 to 5 drops with excellent results and no blank correction in any case. The indicator works well also when the arsenic content of a solution is varied widely. The solution turns green when the indicator is added, and with each succeeding drop of ceric sulfate becomes more blue until a final drop or two of the oxidizing agent causes the whole liquid to turn a deep pink color, which in five to ten seconds changes to a permanent blue shade.

It has been shown in earlier work[4] that the values of the factor obtained by standardizing ceric sulfate against (1) electrolytic iron, (2) sodium oxalate in hot solution, or (3) sodium oxalate at room temperature with iodine chloride as a catalyst were in very close agreement. At this time the conditions for the arsenite–ceric sulfate titration had also been worked out so that it was possible to include these standardizations. A weight buret was used for the ceric sulfate. The experimental conditions for the three methods mentioned above have been given in detail.[4] For the arsenite–ceric salt titration, 0.25-0.30-g. samples of arsenious oxide of very accurately known purity were treated with 1 g. of sodium carbonate and 15 cc. of water and heated gently until solution was complete. The liquid was cooled, diluted with water to about 80 cc., 20 cc. of hydrochloric acid, sp. gr. 1.18, and 5 cc. of iodine chloride were added and the titration was made electrometrically with ceric sulfate. The results are shown in Table III.

TABLE III

WEIGHT NORMALITY FACTOR OF CERIC SULFATE BY DIFFERENT METHODS

Against	(1) Electrolytic Fe, 99.97% Fe. N	(2) $Na_2C_2O_4$ in hot soln., N	(3) $Na_2C_2O_4$ at room temp. ICl as catalyst, N	(4) As_2O_3, 99.985%. N
	0.09410	0.09410	0.09406	0.09381
	.09414	.09416	.09409	.09380
	.09408	.09407	.09409	.09379
	.09408	.09406	.09404	.09381
Average	.09410	,09410	.09407	.09380

The normality factor from the standardization against arsenious oxide is about three parts in a thousand lower than that against electrolytic iron or oxalate, that is, more ceric salt has been required per equivalent weight of reducing agent in the former than in either of the latter cases. Two titrations were made in which the volumes of iodine chloride used were 10 and 15 cc., and the factors obtained were 0.09379 N and 0.09375 N. It would not be expected that the iodine chloride was responsible for the discrepancy as its use in the oxalate-ceric salt titration did not alter the results in the slightest degree. Since oxalate cannot be titrated with ceric sulfate in the presence of either phosphate or fluoride, because of the formation of insoluble salts, possibly double salts, it was thought that arsenate ion might behave in a similar way but the product is so soluble that only a slight error could be introduced. However, the addition of arsenate to either an oxalate solution or an arsenite solution at the beginning of a titration did not alter the volume of ceric salt required. There is as yet no explanation for this result, but from certain observations it seems possible that it may involve formation of double salts with cerium. In using this titration as a method for determining arsenic, accurate results may be obtained either by standardizing the ceric sulfate against arsenious oxide of known purity, or by multiplying the normality factor obtained from an oxalate titration by the correction factor 941/938, that is, 1.003.

V. THE DETERMINATION OF ANTIMONY

In the determination of antimony by an electrometric titration of antimonous chloride with ceric salt, samples of the metal which had been analyzed carefully in connection with atomic weight work[7] were dissolved in hot, concd. sulfuric acid, the cool material diluted with water and concd. hydrochloric acid and solid sodium sulfite added, the excess of sulfur dioxide being removed by boiling. To be certain that a solution thus prepared contained all of the antimony in the trivalent form, a few titrations of such solutions were made electrometrically with potassium bromate, a method shown by Zintl and Wattenberg[8] to be accurate. The potassium bromate solution was made up directly by weight as its oxidizing strength had been accurately determined by comparing it against arsenious oxide of known purity. Zintl and Wattenberg[8] call attention to the fact that it is necessary to make the titration quickly when working with a hot antimonous chloride solution because of oxidation by the air. To eliminate this error, carbon dioxide was used, and the greater part of the ceric sulfate added rapidly from a calibrated pipet and the last few cc. from a 10cc. buret.

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[7] Willard and McAlpine, THIS JOURNAL, 43, 797 (1921).

[8] Zintl and Wattenberg, Ber., 56,472 (1923).

From 0.35–0.45 g. of antimony (99.985%) was dissolved in 5 cc. of hot sulfuric acid, sp. gr. 1.83. To this, when cool, 20 cc. of water, 25 cc. of hydrochloric acid, sp. gr. 1.18, and I g. of sodium sulfite were added. The liquid was left on a low temperature hot-plate for ten minutes, then boiled for the stated time, the evaporated liquid being replaced at intervals by 1:1 hydrochloric acid, then diluted to 100 cc. and titrated electrometrically at 70–80° with 0.1083 *N* potassium bromate. The results are shown in Table IV.

TABLE IV

TITRATION OF ANTIMONOUS CHLORIDE WITH POTASSIUM BROMATE

Time and conditions of boiling to remove excess sulfite	Factor obtained for $KBrO_3$ soln., N
5 minutes while CO_2 bubbled through solution	0.1081
10 minutes while CO_2 bubbled through solution	.1083
20 minutes while CO_2 bubbled through solution	.1084
30 minutes while CO_2 bubbled through solution	.1084
5 minutes no CO_2	.1075
10 minutes no CO_2	.1082
20 minutes no CO_2	.1082
30 minutes no CO_2	.1082

Thus it is seen that theoretical results are obtained by boiling the solution for ten to thirty minutes in a stream of carbon dioxide, and the error is very small if carbon dioxide is not used.

Antimonous chloride solutions, similarly prepared, were cooled to room temperature, iodine monochloride added and titration made electrometrically with ceric sulfate. This titration at room temperature without a catalyst is too slow to be practical. Satisfactory results were not obtained at a higher temperature. Experiments with antimonous chloride solutions containing iodine chloride showed that methylene blue could be used as internal indicator in the titration with ceric salt.

Procedure for Antimony

From 0.35–0.45 g. of antimony was dissolved in 5 cc. of hot sulfuric acid, sp. gr. 1.83. To this, when cool, the stated amounts of water and hydrochloric acid, sp. gr. 1.18, and 1 g. of sodium sulfite were added. The liquid was left on a low temperature hot-plate for ten minutes, then boiled for fifteen minutes while carbon dioxide was bubbled through the solution and the evaporated liquid was replaced at intervals by 1:1 hydrochloric acid, cooled and diluted to 100 cc.; 10 cc. of iodine chloride was added and titration made electrometrically with ceric sulfate, 0.1042 N against sodium oxalate. The results are shown in Table V.

The break at the end-point varied considerably in magnitude, amounting in some cases to 40–50 mv. and in other instances, where the same experimental conditions had been maintained, to as much as 150–180 mv.

TABLE V

TITRATION OF ANTIMONOUS CHLORIDE WITH CERIC SULFATE

H_2O, cc.	HCl, cc.	Sb taken	Sb found
20	25	0.3617	0.3620
		.3708	.3708
		.3804	.3808
30	15	.3778	.3773
		.3362	.3362
		.3709	.3710

per 0.03 cc. of 0.1 N ceric sulfate. The end-point was, however, never difficult to locate.

Summary

1. Arsenious acid may be titrated accurately at 75–85° in hydrochloric acid solution with ceric sulfate, the end-point being determined electrometrically.

2. Potassium bromide may be used as a catalyst in this reaction and the titration made electrometrically either at room temperature or in hot solution. The amount of potassium bromide required for a rapid reaction decreases as the temperature or the hydrochloric acid content of the solution is increased.

3. Iodine has a greater catalytic effect, iodine monochloride being the most convenient form in which to use it, as its presence in a hydrochloric acid solution necessitates no blank correction. With this catalyst, the titration is made at room temperature, the end-point being determined either electrometrically or with methylene blue as an indicator.

4. The normality factor of ceric sulfate obtained by comparison against arsenious oxide is about three parts in a thousand lower than that against oxalate. Therefore, in determining arsenic, the ceric sulfate should be standardized against arsenious oxide of known purity, or a correction be applied to the factor obtained from an oxalate titration.

5. Antimony may be accurately determined by electrometric titration of antimonous chloride with ceric sulfate at room temperature, iodine monochloride being present as catalyst, and the theoretical factor being used.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

CERIC SULFATE AS A VOLUMETRIC OXIDIZING AGENT. VI. THE VOLUMETRIC DETERMINATION OF CERIUM

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Introduction

The persulfate[2] and bismuthate[3] oxidation methods for cerium have remained probably the most accurate as well as the most generally applicable of the many volumetric procedures proposed for this metal. The former method has been tested by a number of investigators,[4] all of whom found it accurate if the experimental conditions suggested by von Knorre were followed closely. The oxidation with persulfate was carried out in a solution containing just enough acid to prevent the precipitation of basic ceric salts, the reaction being

$$H_2S_2O_8 + Ce_2(SO_4)_3 = 2Ce(SO_4)_2 + H_2SO_4$$

If too much acid was present, the oxidation of the cerous salt was incomplete. In the actual procedure, the persulfate was added in three or four portions, the solution boiled after each addition and finally boiled for about fifteen minutes to destroy excess persulfate. Such experimental technique is, obviously, tedious and inconvenient. The oxidation with persulfate has also been carried out in alkaline solution by Sterba-Boehm and Matula,[5] who dissolved the precipitate in potassium iodide and hydrochloric acid and titrated the iodine with thiosulfate, and by Autié,[6] who used nitric acid to dissolve the precipitate and hydrogen peroxide to determine the ceric salt. Either of these procedures involves a number of steps and consistent results were not obtained in the latter method. From this last paper one might be led to think that there were no accurate methods thus far for cerium, as the author's experimental data from a study of a number of volumetric oxidation methods leave much to be desired. Such, however, is not the case. His statement that the reaction of ceric ion with ferrous sulfate is somewhat reversible and that any method based upon this titration is consequently inaccurate, is absurd if one considers the oxidation-reduction potentials of the two systems involved.

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[1] From a dissertation submitted by Philena Young to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Von Knorre, *Z. angew. Chem.*, 11,717 (1897); *Ber.*, 33,1924 (1900).

[3] Metzger, THIS JOURNAL, 31,523 (1909).

[4] (a) Hintz and Weber, *Z. and. Chem.*, *37*, 103 (1898); (b) Power and Sheddon, *J. Soc. Chem. Ind.*, 19, 636 (1900); (c) Marc, *Ber.*, 35, 2370 (1902); (d) Furman, THIS JOURNAL, 50,755 (1928).

[5] Sterba-Boehm and Matula, *Rec. trav. chim.*, 44, 400 (1925).

[6] Autié, *Bull. soc. chim.*, 41, 1535 (1927).

Hydrogen peroxide may be used in this particular titration, as he suggests, but certainly has no advantage over ferrous sulfate in accuracy or stability.

In studying the action of oxidizing agents on cerous salts, Barbieri[7] found that silver nitrate catalyzed in an acid solution the oxidation of cerous nitrate or sulfate with persulfate and used this fact for the purification of crude cerium salts. However, he did not test the possibilities of the method quantitatively. Since his publication investigators have continued to use the original von Knorre method.[4d,5,6,8] The present paper describes the much simpler technique which is possible in the presence of silver ion as catalyst.

Experimental

Titration with Ferrous Sulfate.—The approximately 0.05 N cerous sulfate was prepared from C. P. material and contained 50 cc. of sulfuric acid, sp. gr. 1.83, per liter. Four analyses of 25cc. portions of this solution, using a bismuthate oxidation followed by electrometric titration of the ceric sulfate with standard ferrous sulfate, gave 0.1858, 0.1863, 0.1861 and 0.1858 g. of cerium. Definite amounts of this solution were taken; water, sulfuric acid and silver nitrate (containing 2.5 g. of silver nitrate per liter) were added to a total volume of 200 cc., followed by solid ammonium persulfate. The liquid was boiled for ten minutes, cooled to room temperature and titrated electrometrically with 0.05 N ferrous sulfate which had been standardized against ceric sulfate of known strength. A silver chloride–platinum electrode system was used. The vessel containing the silver chloride electrode in 0.1 N potassium chloride was placed directly in the liquid to be titrated. The quantities of the various materials and the results are shown in Table I.

TABLE I

OXIDATION WITH PERSULFATE–SILVER NITRATE AS CATALYST–TITRATION WITH FERROUS SULFATE

Acid, cc.	$(NH_4)_2S_2O_8$, g.	$AgNO_3$, cc.	*Ce* taken, g.	*Ce* found, g.
2.5 cc. of H_2SO_4, sp. gr. 1.83	1	5	0.1860	0.1863
2.5 cc. of H_2SO_4, sp. gr. 1.83	0.5	5	.1860	low
2.5 cc. of H_2SO_4, sp. gr. 1.83	1	5	.1116	.1118
2.5 cc. of H_2SO_4, sp. gr. 1.83	3	5	.3720	.3722
2.5 cc. of H_2SO_4, sp. gr. 1.83	2	5	.3720	.3719
10 cc. of H_2SO_4, sp. gr. 1.83	2	10	.1860	.1859
10 cc. of H_2SO_4, sp. gr. 1.83	4	10	.1860	.1860
10 cc. of H_2SO_4, sp. gr. 1.83	5	5	.1860	.1858
10 cc. of H_2SO_4, sp. gr. 1.83	5	2.5	.1860	.1856
5 cc. of H_2SO_4, sp. gr. 1.83	2	2.5	.1860	.1860
5 cc. of H_2SO_4, sp. gr. 1.83	4	2.5	.3720	.3722
5 cc. of HNO_3, sp. gr. 1.42	2	2.5	.1860	.1858
10 cc. of HNO_3, sp. gr. 1.42	4	2.5	.1860	.1849
5 cc. of $HClO_4$ (70–72%)	2	2.5	.1860	low

From the data in Table I it is seen that the correct procedure for determining cerium is to use a sulfate solution containing 2.5–10 cc. of sulfuric acid, sp. gr. 1.83, per 200 cc.,

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[7] Barbieri, *Atti* R. *Accad. Lincei*, *25*, *I*, 37 (1916).

[8] Lindeman and Hafstad, *Z. anal. Chem.*, 70, 433 (1927).

or a nitrate solution with 5 cc. of nitric acid, sp. gr. 1.42, in the same volume, add to this 1–5 g. of solid ammonium persulfate, depending on the amount of acid present, 2–5 cc. of silver nitrate (containing 2.5 g. of silver nitrate per liter), boil for ten minutes, cool to room temperature and titrate electrometrically with standard 0.05 *N* ferrous sulfate.

The silver nitrate caused no interference during the titration, the end-point equilibrium was rapid, never more than a few seconds being required for the voltage to become steady and the break in potential averaged 200–250 mv. per 0.03 cc. of 0.05 *N* ferrous sulfate. A variation in volume between 100 and 300 cc. during the oxidation did not alter the results. The remarkable effect ascribed by Lindeman and Hafstad[8] to the presence of a considerable quantity of magnesium sulfate in the solution at the time of a persulfate oxidation was not apparent when silver nitrate was present. The persulfate procedure with silver ion as catalyst is simple and rapid, and has a certain advantage over the bismuthate method in which not only is a filtration required but also a blank determination on the technical bismuthate usually available.[9] Experiments to test the effect of the presence of other rare earths were not made, as the persulfate method has been shown[2,4a,b] to be applicable in such cases.

Titration with Potassium Iodide.—Since ceric nitrate or sulfate may be accurately titrated electrometrically with potassium iodide,[10] such a titration should be possible after a persulfate oxidation if a blank correction is made for the reaction between the silver nitrate and the iodide. To test this point, 15cc. portions of a ceric sulfate solution were taken, treated with 2.5 cc. of sulfuric acid, sp. gr. 1.83, and water to a volume of 200 cc. The stated amounts of silver nitrate (containing 2.5 g. of silver nitrate per liter) were added and the solution was titrated electrometrically with an approximately 0.05 *N* potassium iodide solution which had been standardized against ceric sulfate of known strength. The results are shown in Table II.

TABLE II

IODIDE TITRATION OF CERIC SULFATE—SILVER NITRATE PRESENT

No.	$AgNO_3$, cc.	NaCl, cc.	KI, 0.05 N, cc.	Blank actual	Blank calcd.
1	0	0	24.33–24.32	0.00	0.00
2	1	0	24.61	.28	.27
3	2	0	24.89	.56	.54
4	4	0	25.43	1.10	1.09
5	6	0	25 96	1.63	1.63
6	2	2	24.89	0.56	..
7	2	5	24.88	.55	..

The sodium chloride solution added before the titration in the last two experiments was of the same normality as the silver nitrate solution. The results for these two experiments show that the silver chloride is converted quantitatively into silver iodide during the titration. The values for the calculated blanks were obtained by considering the actual blank in Experiment 5 as correct and taking the proper aliquot portions of this value for the other blanks. The very close agreement between the actual and calculated blanks shows that the correction to be applied is strictly proportional to the amount of silver nitrate in solution.

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[9] Someya, Z. *anorg. Chem.*, **168**, 56 (1927), states that a filtration is unnecessary, but he used a very pure grade of bismuthate in his work. He found, however, that he had to wait three to five minutes at the equivalent point for equilibrium to be established.

[10] Willard and Young, THIS JOURNAL, 50, 1368 **(1928).**

Twenty-five cc. portions of the cerous sulfate used in Table I were diluted with water and acid to 200 cc., the persulfate oxidation was carried out in the presence of a measured amount of silver nitrate and the ceric sulfate and silver nitrate were titrated electrometrically with the same 0.05 N potassium iodide used in the experiments in Table II. The weight of cerium present was 0.1860 g. The results are shown in Table III.

TABLE III

OXIDATION WITH PERSULFATE–SILVER NITRATE AS CATALYST—TITRATION WITH POTASSIUM IODIDE

No.	H_2SO_4, sp. gr. 1.83, cc.	$(NH_4)_2S_2O_8$, g.	$AgNO_3$, cc.	KI, 0.05 *N*, cc.	Blank, actual, cc.	Ce, g.
1	2.5	1	2	23.23	0.55	0.1862
2	2.5	1	4	23.78	1.10	.1862
3	2.5	1	1	less than 21 cc.	...	...
4	5 cc. HNO_3, sp. gr. 1.42	2	2	23.21	0.55	.1860

The actual blank correction for the silver nitrate was obtained by considering the difference between the volumes in Experiments 1 and 2, or 0.55 cc. as the volume of potassium iodide required by 2 cc. of silver nitrate solution. The amounts of cerium found in the 25cc. portions of the cerous sulfate solution agree very closely with the results in Table I as well as with the bismuthate analyses. The break in potential amounted to 100–150 mv. per 0.03 cc. of 0.05 N potassium iodide.

Titration with Sodium Nitrite.—The possibility of using sodium nitrite as the reducing agent for ceric ion after a persulfate oxidation was investigated. Measured portions of a standard ceric sulfate solution were taken, diluted with water and acid to a volume of 200 cc. and titrated electrometrically with 0.1 N sodium nitrite, the greater portion being added from a pipet beneath the surface of the liquid, the remainder in a similar way from a 10cc. buret. The temperature of the solution was 40–45°. The results are shown in Table IV.

TABLE IV

NITRITE TITRATION OF CERIC SULFATE

$Ce(SO_4)_2$, 0.1 *N*, cc.	Acid, cc.	$NaNO_2$, 0.1 *N*, cc.
20	5 cc. of H_2SO_4, sp. gr. 1.83	17.18
20	10 cc. of H_2SO_4, sp. gr. 1.83	17.15
20	20 cc. of H_2SO_4, sp. gr. 1.83	17.23
50	5 cc. of H_2SO_4, sp. gr. 1.83	42.82
20	5 cc. of HNO_3, sp. gr. 1.42	17.12
20	10 cc of HNO_3, sp. gr. 1.42	17.12
20	15 cc. of HNO_3, sp. gr. 1.42	17.12
50	10 cc. of HNO_3, sp. gr. 1.42	42.82
10	10 cc. of HNO_3, sp. gr. 1.42	8.56

The results were not quantitative in perchloric acid solution. The equilibrium in the region of the end-point was very slow in sulfuric acid solution and slightly more rapid in nitric acid solution. The break in potential averaged 50–100 mv. in the former and 150–200 mv. in the latter cases per 0.03 cc. of 0.1 *N* sodium nitrite. With a temperature of 60°, the equilibrium at the end-point was somewhat more rapid and the values were not altered.

Two procedures were used for standardizing the nitrite solution: that of Busvold[11] depending on the reduction of silver bromate by nitrite and the weighing of the silver bromide formed, and that of Lunge[12] based on the titration of standard permanganate with nitrite. Laird and Simpson[13] tested both of these methods and found the gravimetric procedure accurate. In the volumetric method their results were not so exact, but they state that with sufficient care accurate results could probably be obtained. A series of preliminary titrations of 0.1 N potassium permanganate with 0.1 N sodium nitrite in solutions containing 10 cc. of sulfuric acid, sp. gr. 1.83, per 200 cc. showed that closely checking duplicates could be obtained and that the volume of nitrite solution varied strictly with the amount of permanganate used, if the precaution of adding the nitrite beneath the surface of the liquid was observed.

An approximately 0.1 *N* sodium nitrite solution was prepared from material containing only 0.002% of chloride. (1) 0.8 g. of silver bromate was dissolved in 200 cc. of water in a 500cc. flask at **80–85°**, 100 cc. of the nitrite solution added from a pipet, followed by 30cc. of sulfuric acid, sp. gr. 1.2, the liquid being shaken thoroughly at this time and at frequent intervals to coagulate the silver bromide. After standing for three to four hours on the edge of the hot-plate, the precipitate was filtered, washed thoroughly with hot water and dried to constant weight. The same results were obtained when the silver bromate was dissolved in 2 N acetic acid,[11] provided that acetic acid distilled from chromic acid was used. With the ordinary c. p. acetic acid. the results were high, probably due to the presence of formic acid. (2) Fifty cc. portions of 0.06901 N permanganate, standardized against sodium oxalate, were treated with 165 cc. of water and 10 cc. of sulfuric acid, sp. gr. **1.83.** Twenty-five cc. of nitrite solution was added from *a* pipet beneath the surface of the liquid; the solution was then heated slowly while the remainder of the nitrite was added in a similar way from a 10cc. buret. The end-point was determined electrometrically and the final temperature was 50–55°. (3) Twenty-five cc. portions of 0.09488 N ceric sulfate, standardized against sodium oxalate, were treated with 170 cc. of water and 50 cc. of nitric acid, sp. gr. 1.42, and titrated electrometrically at 40–45° with sodium nitrite, using the technique described above. The results are shown in Table V.

These data indicate that accurate results may be obtained in the titration of permanganate with a reducing agent, a procedure which has been much debated, and the authors intend to investigate the permanganate–nitrite reaction in greater detail.

[11] Busvold, *Chem.-Ztg.*, **38,** 28 (1914).

[12] Lunge, *Ber.*, **10,** 1073 (1877).

[13] Laird and Simpson, THIS JOURNAL, 41, **524** (1919).

TABLE V

STANDARDIZATION OF SODIUM NITRITE SOLUTION

Method of standardization	Normality factor	Average
Gravimetric	0.1064, 0.1061, 0.1062 .1063	0.1062
Titration of standard permanganate	.1064, .1064, .1064	.1064
Titration of standard ceric sulfate	.1064, .1064	.1064

An accurate procedure for nitrite, based upon the addition of the nitrite solution to excess of standard ceric sulfate, followed by titration of the excess of the oxidizing agent with standard ferrous sulfate or potassium iodide, is obvious from the above experimental work.

Determination of Cerium

Twenty-five cc. portions of the cerous sulfate solution used in Table I were diluted with water and 5 cc. of nitric acid, sp. gr. 1.42, to 200 cc., and the persulfate oxidation in the presence of silver nitrate was carried out in the usual way, The ceric sulfate was titrated electrometrically at 40–45° with the sodium nitrite standardized above. Three analyses gave 0.1855, 0.1859, 0.1859 g. of cerium, a close agreement with the average value 0.1860 *g.* of cerium from bismuthate oxidations.

Attempts to titrate the ceric sulfate with oxalate in hot solution in the presence of silver nitrate after having boiled the liquid for ten minutes to remove excess persulfate were not very satisfactory. The equilibrium was reached very slowly in the region of the end-point and the volume of oxalate required was slightly larger with silver nitrate present, but not proportional to the amount of this latter material, If the ceric sulfate solution was cooled to room temperature, considerable hydrochloric acid and 5 cc. of 0.005 N iodine chloride added, the titration with oxalate seemed to proceed rapidly but no end-point break could be obtained.

A few experiments were made to test the quantitative possibilities of two methods suggested by Barbieri:[7] (1) titration of cerous salt in strong sulfuric acid solution with permanganate, and (2) a similar titration in a dilute acid solution containing phosphoric acid. A visual end-point was impossible in the first method, due to the color of the ceric salt, and very difficult to obtain with even fair accuracy in the second method. A potentiometric end-point was impossible in either case, the sligbt solubility of the ceric phosphate probably being the source of trouble in the second method.

Summary

1. Cerium may be accurately determined in the presence of the other rare earths by oxidation with persulfate in the presence of silver nitrate as catalyst, followed by electrometric titration with standard ferrous sulfate, potassium iodide or sodium nitrite. Hydrogen peroxide offers no advan-

tages in accuracy or stability of solution. The procedure in this oxidation method is much simpler and more rapid than that required in the original von Knorre persulfate method.

2. With potassium iodide a blank correction must be subtracted from the volume used because of the action between the silver and iodide ions.

3. With sodium nitrite the equilibrium in the region of the end-point is quite slow. The sodium nitrite solution, if practically free from chloride, may be standardized gravimetrically by weighing the silver bromide formed from the action between silver bromate and nitrite in acid solution. A .alternative method is the electrometric titration of standard potassium permanganate with the nitrite solution.

ANN ARBOR, MICHIGAN

NOTE

An Improved Test for Borates.—A solution suspected of containing a borate is made slightly alkaline with sodium hydroxide and evaporated practically to dryness. The residue is treated with 1 *cc.* of concentrated sulfuric acid and allowed to cool. Two cc. of methanol is then added and the solution transferred to a test-tube. The latter is fitted with a two-holed rubber stopper through which two glass tubes of about 4 mm. bore are inserted. One of these tubes extends to the bottom of the test-tube, and the external portion of it is bent to an angle convenient to allow its use as a mouthpiece. The other tube serves to conduct the vapors from the test-tube and therefore does not extend far below the rubber stopper. The external portion contains a right angle bend and terminates in a long capillary. This capillary should be at least 3 cm. long and should have a bore not greater than 0.5 mm.

When air from the lungs is blown into the apparatus the bubbles arising through the heated solution convey the volatile methyl borate (if present) out through the capillary tube. The exit stream of vapors is directed into a small, non-luminous Bunsen flame. A characteristic green color will be produced in the Bunsen flame if a borate is present in the original solution.

The long capillary of the exit tube prevents any flame from traveling back into the test-tube and at the same time concentrates the effect in the Bunsen flame.

As little as 0.2 mg. of boric acid has been detected by this test.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY
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RECEIVED FEBRUARY 2, 1928
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

BIOCHEMISTRY OF SULFUR. II. THE ISOLATION OF ERGOTHIONEINE FROM ERGOT OF RYE

BY BLYTHE A. EAGLES[1]

RECEIVED MAY 3, 1927 PUBLISHED MAY 5, 1928

In the previous paper from this Laboratory, it was shown by Eagles and Johnson[2] that sympectothion[3,4,5] and thiasine[6,7] from pig's blood were identical with ergothioneine from ergot of rye. It has also been reported and shown independently by Newton, Benedict and Dakin[8,9] that thiasine is identical with ergothioneine.

A renewed interest in the biochemistry of organic sulfur combinations has been created as a result of these researches. Eagles and Johnson isolated ergothioneine from ergot of rye for purposes of comparison with that obtained from pig's blood. The method adopted for the isolation and final purification of this sulfur compound from ergot of rye differed from the original method of C. Tanret[10] or the later one of G. Tanret.[11] Any improvement in technique that can be recommended for the separation and isolation of this substance from natural sources deserves especial attention. The original procedure of Tanret was followed up to the separation of the compound as the mercuric chloride salt. Instead of isolating the compound as the hydrochloric acid salt at this stage, the procedure of Hunter and Eagles[4,5] for its isolation from blood was then used and the substance isolated in the pure state as the free base.

The procedure will be described in detail.

Experimental

One kg. of finely ground ergot of rye[12] was extracted in a Soxhlet apparatus with 90% alcohol for four hours; 300 cc. of alcohol per 100 g. of powder was used. The residues were twice boiled with one-half the volume of alcohol, filtered through cheesecloth and the filtrate combined with the original extract. Alcohol was distilled from

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[1] Holder of a Sterling Research Fellowship in Chemistry at Yale University, 1926–27.

[2] Eagles and Johnson, THIS JOURNAL, 49, 575 (1927).

[3] Bulmer, Eagles and Hunter, J. *Biol. Chem.*, 63, 17 (1925).

[4] Hunter and Eagles, *ibid.*, 65, 623 (1925).

[5] Hunter and Eagles, *ibid.*, 72, 123 (1927).

[6] Benedict, *ibid.*, 64, 215 (1925).

[7] Benedict, Newton and Behre, *ibid.*, 67, 267 (1926).

[8] Newton, Benedict and Dakin, *Science*, 64, 602 (1926).

[9] Newton, Benedict and Dakin, *J. Biol Chem.*, 72, 367 (1927).

[10] Tanret, J. *pharm. chim.*, [VI] 30, 145 (1909).

[11] Tanret, *Bull. soc. chim.*, 31, 444 (1922).

[12] For the supply of ergot of rye necessary for the isolation of ergothioneine, we wish to express our thanks to the Upjohn Company of Kalamazoo, Michigan, and Sharp & Dohme of Baltimore, Maryland.

the extract, water added and the separated fats and resins were removed by filtration. The volume of solution was then 2200 cc. Considerable coloring matter was removed with barium hydroxide, leaving the solution acid to litmus Basic lead acetate[13] was then added to maximum precipitation (94 cc. required) and the precipitate centrifuged. Excess lead was removed from the filtrate by sulfuric acid. It was then made alkaline to phenolphthalein with 2.5 N sodium hydroxide for the extraction of alkaloids with chloroform. The solution was then acidified with acetic acid and warm 8% aqueous mercuric chloride added to maximum precipitation. This corresponds to the mercuric chloride precipitation used by Hunter and Eagles in the isolation of ergothioneine from pig's blood. The mercury salt of ergothioneine was well washed with 0.25% aqueous mercuric chloride, suspended in 100 cc. of water and the mercury removed with hydrogen sulfide. After the separation of mercuric sulfide, Tanret then isolated ergothioneine as the hydrochloric acid salt. On account of the high solubility of this salt, it was thought advisable to continue further fractionation of the product and attempt its isolation as the free base. The technique used by Hunter and Eagles for its isolation from blood was followed. The filtrate from mercuric sulfide was freed from hydrogen sulfide by aeration and subjected to the lead acetate-sodium hydroxide precipitation. The volume of filtrate was 146 cc. and required for practically complete precipitation of ergothioneine 61 cc. of 20% sugar of lead, 27.5 cc. of 2.5 N sodium hydroxide and 8 cc. of 10% sodium chloride. After freeing from its lead salt with sulfuric acid, it was precipitated with phosphotungstic acid and then isolated as the free base; 0.65 g. of pure ergothioneine was obtained.

This method of isolation may be considered an improvement on those of C. and G. Tanret in that it consists in the addition to those methods of two precipitations which serve to separate ergothioneine from impurities present and has the further advantage that the compound is obtained directly as the free base rather than as its hydrochloric acid salt. The yield is much higher than any previously recorded.

I wish to express my great indebtedness to Professor Treat B. Johnson for his kindly advice and help throughout this work.

Summary

An improved method of isolating ergothioneine from ergot of rye has been detailed.

NEW HAVEN, CONNECTICUT

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[13] Goulard's Extract, United States Pharmacopeia IX, Philadelphia, 1916, 249.

[Contribution from the Chemical Laboratory of Clark University]

REACTIONS OF STRONGLY ELECTROPOSITIVE METALS WITH ORGANIC SUBSTANCES IN LIQUID AMMONIA SOLUTION. VI. A. THE REDUCTION OF BENZOPHENONE. B. THE HYDROLYSIS OF METAL KETYLS[1]

By Charles Bushnell Wooster

Received September 22, 1927 Published May 5, 1928

In 1891 E. Beckmann and T. Paul[2] found that certain aromatic ketones reacted with sodium in the proportion of one atom of metal to one molecule of ketone, forming highly colored addition products. Later, Schlenk and his co-workers[3] confirmed this result. A molecular weight determination by the ebullioscopic method enabled them to prove that the potassium derivative of phenylbiphenyl ketone was monomolecular in solution. Schlenk, therefore, proposed the name "metal ketyls" for this new class of substances represented by the general formula, $R_2{=}\overset{/}{C}{-}ONa$. He also found that disodium derivatives could be prepared by further action of the metal.

These reactions, which were carried out in benzene or ethereal solutions and in a nitrogen atmosphere, took place rather slowly. Following an observation of Kraus and White,[4] an investigation was undertaken of the reaction of sodium with benzophenone in liquid ammonia solution. It was found that this reaction occurred readily and rapidly. Either a mono- or disodium derivative could be obtained at will by merely adding the correct proportion of sodium. The compound containing two atoms of metal yields deep purple solutions in liquid ammonia and a considerable difference in the relative reactivity of the two sodium atoms was observed. Naturally, the sodium atom directly attached to a carbon atom is far more readily removed than that attached to oxygen, but this difference is enhanced by the fact that the latter atom exhibits even less reactivity than would be expected. This is evident in the reaction with excess ethyl bromide in which only one of the metal atoms is directly substituted.

$$(C_6H_5)_2CNaONa + C_2H_5Br \longrightarrow (C_6H_5)_2C(ONa)C_2H_5 \qquad (1)$$

$$(C_6H_5)_2C(ONa)C_2H_5 + C_2H_5Br + NH_3 \longrightarrow (C_6H_5)_2COHC_2H_5 + C_2H_5NH_2 + NaBr \qquad (2)$$

The second reaction probably takes place through the intermediate formation of ethylammonium bromide.

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[1] A portion of this material was submitted in a thesis for the degree of Master of Arts at Clark University, 1925.

[2] Beckmann and Paul, *Ann.*, 266, 1 (1891).

[3] (a) Schlenk and Weickel, Ber., 44, 1182 (1911); (b) Schlenk and Thal, *ibid.*, 46, 2840 (1913).

[4] Kraus and White, This Journal, 45, 771 (1923).

An entirely different type of reaction occurred when disodium benzophenone was treated with phenyl iodide.

$$(C_6H_5)_2CNaONa + C_6H_5I + NH_3 \longrightarrow (C_6H_5)_2C(NH_2)ONa + C_6H_6 + NaI \qquad (3)$$

One product, sodium a-aminobenzhydrolate, is decomposed by water.[5]

$$(C_6H_5)_2C(NH_2)ONa + H_2O \longrightarrow NaOH + NH_3 + (C_6H_5)_2C{=}O \qquad (4)$$

All of the final products indicated were actually obtained.

The partition of a molecule of ammonia between two radicals is a very common occurrence in liquid ammonia solution. In the present instance, the novel feature is that the partition takes place exclusively between two *different* groups, all the hydrogen reducing phenyl groups and all the amino radicals combining with metal ketyl groups rather than with some of the phenyl radicals to form aniline, diphenylamine or triphenylamine as always occurs when only the latter are present!

A potassium derivative of benzophenone which is similar to the disodium compound results not only upon interaction of metal and ketone but also when benzhydrol is treated with potassium amide.

$$(C_6H_5)_2CHOH + KNH_2 \longrightarrow (C_6H_5)_2CHOK + NH_3 \qquad (5)$$

$$(C_6H_5)_2CHOK + KNH_2 \longrightarrow (C_6H_5)_2CKOK + NH_3 \qquad (6)$$

The second reaction demonstrates the acidic character of the methane hydrogen atom in potassium benzhydrolate. It is analogous to the action of potassium amide on triphenylmethane.[7]

In accordance with the views of Schlenk, the monosodium derivative appears to be a typical free radical. It is noteworthy that its reactions are predominately of the addition type, and in the second section of this paper evidence is presented to indicate that the general, if not exclusive, occurrence of such reactions is a characteristic of this substance. It appears that even the decomposition of these extremely unstable alkali metal compounds by water and strong acids (ammonium chloride in liquid ammonia solution) is preceded by the formation of addition compounds.

Experimental Part

The reactions were carried out in an apparatus similar to that which has already been described in an earlier number of this series.[6]

The **Disodium Derivative of Benzophenone.**—Both reacting constituents are soluble, as is also the product. Reaction appears to follow the equation

$$(C_6H_5)_2C{=}O + 2Na \longrightarrow (C_6H_5)_2CNaONa \qquad (7)$$

The sodium atoms may be replaced with hydrogen through the action of either ammonium chloride or water. In the first case, immediate decolorization occurs, whereas when water is employed, a transient greenish coloration is evident. **Benzhydrol, $(C_6H_5)_2CHOH$,** was obtained in both experiments and was characterized by its melting

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[5] Haller and Bauer, *Ann. chim. phys.*, 16, 145 (1909).

[6] White, THIS JOURNAL, 45, 779 (1923).

[7] Kraus and Rosen, *ibid.*, 47, 2741 (1925).

point, by the deep red coloration given with sulfuric acid and also by oxidation to benzophenone. In one hydrolysis the sodium compound obtained from **3.95** g. of benzophenone yielded **3.90** g. of benzhydrol, indicating practically quantitative transformation.

Oxygen and sulfur act readily upon disodium benzophenone with regeneration of the free ketone.

Action of Ethyl Bromide on **Disodium Benzophenone.**—Ethyl bromide reacts with disodium benzophenone in liquid ammonia, giving a white precipitate and a light yellow solution. The residue was extracted with anhydrous organic solvents and a substance was obtained which melted at 92.5° after recrystallization. This was identified as diphenylethyl carbinol by analysis. Calcd.: C, **84.9;** H, **7.55;** mol. wt., **212.** Found: C, **81.3;** H, **7.54;** mol. **wt., cryoscopic** in benzene, **210.8.8** and by means of a reaction described by Hell and Bauer,[9]

$$(C_6H_5)_2COHC_2H_5 + (CH_3CO)_2O \longrightarrow 2CH_3COOH + (C_6H_5)_2C{=}CHCH_3 \qquad (8)$$

2.2 g. of compound yielded **0.53** g. of pure **α,α-diphenylpropene,** melting at 52°.

Prolonged action of ethyl bromide in large excess did not form an ether, $(C_6H_5)_2C(C_2H_5)OC_2H_5$, but only the free alcohol. Hydrolysis of the intermediate product, $(C_6H_5)_2CONaC_2H_5$, was excluded by analysis of the inorganic residue, which proved to be pure sodium bromide. (0.5554 and **0.3724 g.** samples required 54.87 and **37.67** cc. of **0.09974** N silver nitrate, equivalent to **0.5637** and **0.3897** g. of sodium bromide, respectively.) **3.95** g. of benzophenone was then treated with **1.0** g. of sodium and **3.53** cc. of ethyl bromide. The ammonia was distilled under dilute hydrochloric acid. This solution was evaporated to dryness and the residue **(350** g.) extracted with **95%** alcohol. The residue from this extract was extracted with absolute alcohol. From this solution **0.81** g. of ethylamine hydrochloride was isolated (calcd.: **1.78** g.).

The reaction expressed in Equation **2** was confirmed with potassium diphenylethyl carbinolate. This was prepared from **3.59** g. of the alcohol in liquid ammonia.

$$(C_6H_5)_2COHC_2H_5 + KNH_2 \longrightarrow (C_6H_5)_2COKC_2H_5 + NH_3 \qquad (9)$$

It appeared as a white precipitate but was readily dissolved by ethyl bromide; **3.1** g. of the free alcohol was recovered but no trace of an ether was found.

Action of Phenyl Iodide on Disodium Benzophenone.—Bromobenzene was inactive but phenyl iodide reacted readily. The residues from three reactions when severally treated with water and extracted with organic solvents yielded only benzophenone and in amounts suggesting it as a principal product. Formation of aniline, di- or triphenylamine was excluded by separate qualitative tests of the aqueous extract and by proving nitrogen absent from the ether extract. When the solvent ammonia was distilled under water a little benzene was collected.

The reaction residue was then examined directly. The product from **1.5** g. of sodium, 5.77 g. of benzophenone and excess phenyl iodide was thoroughly washed with hot toluene, hot benzene and petroleum ether and then dried in a vacuum desiccator. When a portion was boiled with water, benzophenone separated and ammonia was detected in the escaping vapors with mercurous nitrate paper. After complete expulsion of ammonia, the solution still reacted alkaline and also gave a test for iodide ions.

The Action of Potassium Amide on **Benzhydrol.**—One and 68 hundredths g. of potassium was converted into potassium amide in liquid ammonia and treated **with 2** g. of benzhydrol. The solution of the potassium alcoholate was light orange in color and transparent but began to turn greenish after ten to fifteen minutes, finally becoming deep purple and opaque at the end of twenty hours. A stream of dry air decolorized

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[8] **Buxton,** Thesis. Clark University, **1924;** Everett H. Gibbs, unpublished observations.

[9] Hell and Bauer, ***Ber.*, 37,231 (1904).**

the mixture but upon standing the purple color characteristic of dipotassium benzophenone was regenerated.

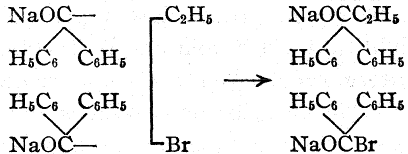
The Monosodium Derivative of Benzophenone.—When one equivalent of sodium was added to a solution of benzophenone in liquid ammonia, reaction occurred and a deep blue solution resulted. The presence of a definite monosodium compound was demonstrated by an experiment employing 3.95 g. of benzophenone and 0.5 g. of sodium. The residue was repeatedly extracted with hot petroleum ether. This extract was filtered in an atmosphere of ammonia and evaporated, The amount of benzophenone resulting represented the quantity present as such in the reaction product plus that formed by inadvertent oxidation during the extraction. Only 0.06 g. was obtained.

Excess ammonium chloride immediately decolorized the blue solution. Extraction of the residue with benzene yielded a product which was resolved by fractional crystallization from petroleum ether into benzhydrol (m. p. 67°) and benzophenone (m. p. 48°). No trace of benzopinacone was detected. When water was employed, a transient green color appeared but the same products resulted.

These products are analogous to those obtained from monopotassium phenylbiphenyl ketone and other metal ketyls.[3a]

Beckmann and Paul[2] reported that benzopinacone is also produced by hydrolysis of monosodium benzophenone. That it was formed in liquid ammonia, even as an intermediate product, is very improbable since it should be stable under these conditions and those prevailing during purification.

The Action of Ethyl Bromide on Monosodium Benzophenone—This reaction yields sodium bromide, a yellow solution and a separate, orange-colored liquid phase. The benzene extract of the reaction residue gave upon evaporation a yellow liquid that did not solidify when cooled in a mixture of ice and salt. Qualitative tests showed the absence of nitrogen and halogen. It was twice distilled under reduced pressure. The residue in the distilling flask deposited, upon standing, some crystals of diphenylethyl carbinol (m. p., 93°). The apparent molecular weight (cryoscopic in benzene) of the distillate was 182, indicating that benzophenone was the principal constituent. This was obtained in crystalline form and identified after cooling the liquid to −33.5° and inocculating with the ketone. The reaction probably follows the equations[S']



(10)

$$(C_6H_5)_2C(Br)ONa \longrightarrow (C_6H_5)_2C{=}O + NaBr \qquad (11)$$

$$(C_6H_5)_2CONaC_2H_5 + C_2H_5Br + NH3 \longrightarrow (C_6H_5)_2COHC_2H_5 + C_2H_5NH_2 + NaBr \qquad (12)$$

B. The Hydrolysis of Metal Ketyls

A Sodium Ammonium Derivative of Benzophenone.—Kraus and Kawamura[10] observed that the reaction between sodium triphenylmethide and ammonium chloride in liquid ammonia yields the corresponding ammonium compound as a pinkish precipitate. It slowly decomposes, even at −33.5°, to form triphenylrnethane and ammonia.

In the reaction of disodium benzophenone with excess ammonium chloride, decolorization was practically instantaneous and any interme-

[10] Kraus and Kawamura, THIS JOURNAL, 45,2758 (1923).

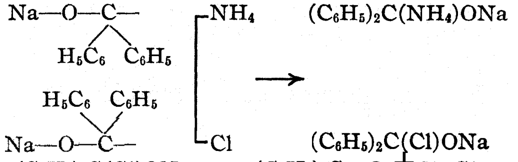
diate compound, if formed, must have been very unstable. This result is to be expected, since the compound formed under these conditions would contain two ammonium groups and would in consequence be much less stable than ammonium triphenylmethide. If it were possible to replace but one of the sodium atoms with an ammonium group, a more stable product could be expected. For this purpose, the disodium compound prepared from 1.82 g. of ketone and 0.46 g. of sodium was treated with 0.54 g. of ammonium chloride, this amount being equivalent to one-half of the sodium. The purple solution immediately became nearly blue in color and the reflected light was no longer green. If the reagent had reacted with all of the sodium in one-half the total amount of compound present, the color of the remaining solution should then be that of disodium compound at one-half the original concentration; but a previous experiment had shown this to be purple and quite stable for at least twenty-seven hours. Apparently, the more active sodium atoms were all replaced with ammonium groups

$$(C_6H_5)_2C(Na)ONa + NH_4Cl \longrightarrow NaCl + (C_6H_5)_2C(NH_4)ONa \qquad (13)$$

After a lapse of eight and one-half hours, the solution became light yellow and transparent. This confirmed Equation **13,** for disappearance of the blue color was caused by decomposition of the unstable sodium ammonium compound

$$(C_6H_5)_2C(NH_4)ONa \longrightarrow (C_6H_5)_2CHONa + NH_3 \qquad (14)$$

Intermediate Reactions of Monosodium Benzophenone and Ammonium Chloride.—Since excess ammonium chloride immediately decolorized solutions of monosodium benzophenone, the monoammonium derivative, if formed, must also be very unstable. Other explanations of this reaction may be given. Immediate replacement of the sodium atom by hydrogen might take place, followed by reaction with the solvent ammonia or by the intermolecular oxidation and reduction suggested by Schlenk and Weickel.[3a] On the other hand *addition* of ammonium chloride might occur, so that the sodium ammonium compound would be formed



(15)

$$(C_6H_5)_2C(Cl)ONa \longrightarrow (C_6H_5)_2C{=}O + NaCl \qquad (16)$$

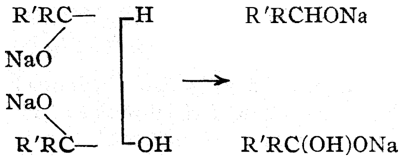
$$(C_6H_5)_2C(NH_4)ONa + NH_4Cl \longrightarrow NaCl + (C_6H_5)_2CHOH + 2NH_3 \qquad (17)$$

It is evident from Equations 15, 16 and 17 that the sodium ammonium compound should result if the third reaction was eliminated by using an amount of ammonium chloride equivalent to but one-half of the sodium. Accordingly, an experiment was made with 0.23 g. of sodium, 1.82 *g.* of **ketone** and 0.27 *g.* of ammonium chloride. **A** small quantity of dry ether was added to hold any regenerated benzophenone in solution; otherwise it separates as a gummy mass and retards the color changes. The blue color of the solution remained apparently unchanged immediately after the addition of ammonium chloride, but then slowly faded until it had entirely disappeared at the end of seven hours. The theory expressed in Equations 15, 16 and 17 was thus confirmed, for the other explanations predict an abrupt and marked diminution of color due to decreased concentration of monosodium compound, after which the color should be stable for at least twenty-seven hours, as has been proved in a separate experiment. The reaction expressed in Equation 15 is particularly noteworthy since ammonium chloride behaves as a strong acid in liquid ammonia solution.

Hydrolysis of Metal **Ketyls.**—Hydrolysis of the sodium compounds in liquid ammonia may be considered analogous to the reaction with ammonium chloride. However, since ammonium hydroxide is more weakly acidic than ammonium chloride, the reaction of the sodium ammonium compound with excess reagent would be expected to proceed somewhat slowly and decolorization would be retarded. In fact, a green coloration was observed in all cases. This indicates the presence of sodium ammonium compound which would appear green at low concentration, since the final reaction mixture is always light yellow.

Some inferences may also be drawn regarding the course of hydrolysis under other conditions. Schlenk and Weickel[3a] have already suggested that immediate replacement of the sodium by hydrogen occurs, followed by polymerization or intermolecular oxidation and reduction, or both, depending upon the nature of the metal ketyl. However, it is difficult to understand why the radical, R'RC—OH, should undergo intermolecular oxidation and reduction instead of simple polymerization when the polymer is stable under the conditions of the experiment and no other factor, such as reaction with solvent, is involved. Yet no polymer was obtained by Schlenk and his co-workers from any of the numerous metal ketyls which they prepared and hydrolyzed. The only exceptions were observed by Beckmann and Paul, as has been previously mentioned.

Since it appears that intermediate addition products result between the metal ketyls and either moderately electropositive groups (NH_4) or weakly amphoteric radicals (C_2H_5), there is little reason to believe that the hydrogen atom, occupying an intermediate position, would not behave similarly. Consequently, the following general reaction scheme may be proposed



(18)

$$R'RC(OH)ONa \longrightarrow R'RC{:}O + NaOH \qquad (19)$$
$$R'RCHONa + H_2O \longrightarrow R'RCHOH + NaOH \qquad (20)$$

Formation of a pinacone, as observed by Beckmann and Paul, would imply that the sodium compound was itself partially polymerized under the conditions of their experiment and that direct hydrolysis of this polymer occurred to some extent.

The author wishes to acknowledge his deep obligation to Dr. George F. White, at whose suggestion this research was initiated, and to thank the other members of the Faculty of the Department of Chemistry of Clark University for their aid.

Summary

1. Both mono- and disodium derivatives of benzophenone may be prepared readily by the action of sodium in liquid ammonia. Dimetallic derivatives may also result from the action of amides on the corresponding alcohol.

2. The reactions of ethyl bromide and phenyl halides with sodium compounds of benzophenone have been studied. Both substitution and reactions involving the solvent have been observed.

3. Evidence has been presented to show that the occurrence of addition reactions is a more general property of the metal ketyls than has been previously supposed. Even their decomposition by strong acids may be preceded by the formation of addition products.

CAMBRIDGE, MASSACHUSRTTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HAMLINE UNIVERSITY]

ALIPHATIC-AROMATIC ARSENO COMPOUNDS. II. β-HYDROXYETHYLARSONIC ACID AND SOME ARYL ARSENO-ETHANOLS[1]

BY R. HERBERT EDEE

RECEIVED NOVEMBER 25, 1927 PUBLISHED MAY 5, 1928

A complete series of unsymmetrical aliphatic-aromatic arseno compounds has been described in the literature.[2] In this series it was found that all of the members were soluble because of the presence of a carboxyl group in the aliphatic part of the molecule. Most of the compounds contained additional solubilizing groups in the aromatic part. It was thought desirable to prepare a series of aliphatic-aromatic arseno compounds whose solubilities would be due to the presence of certain groups in the aromatic portion of the molecule. The series to be described contains the hydroxy-ethyl group, $-CH_2CH_2OH$, as the aliphatic portion and various aryl groups as the aromatic part of the arseno molecule.

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[1] This paper is the result of an investigation which was begun at the suggestion of Dr. Charles Shattuck Palmer, formerly of Northwestern University.

[2] Palmer and Edee, THIS JOURNAL, 49, 998 (1927).

The first step in this investigation was the preparation of β-hydroxyethylarsonic acid. This acid is mentioned in the literature,[3] but the evidence shows that it has never been prepared in the pure state. By the procedure which was followed a solution containing 85% of β-hydroxyethylarsonic acid was prepared. The only impurities present were found to be water and alcohol. Since neither of these substances influences the reduction of the acid with the subsequent formation of arseno compounds, the preparation of pure aryl arseno-ethanols from this solution was possible. A solution of the acid which had stood in a vacuum over sulfuric acid finally crystallized in large leaflets and gave an analysis which was correct for the pure acid containing one molecule of water of crystallization. It was found impossible to isolate the acid in the form of any of its metallic salts as these are all extremely soluble and decompose on evaporation of their solutions.

In general, the method used in the preparation of the arseno-ethanols consisted in adding the reducing agent, hypophosphorous acid, to $M/50$ portions of the aromatic acid and the β-hydroxyethylarsonic acid in rather strong hydrochloric acid solution. The filtered solution was then placed in the cold for varying lengths of time. As a rule the arseno compound separated and could be washed and dried. Different aromatic acids, however, were found to require variations in this procedure. As in the case of the arseno-acetic acids, the arseno-ethanols are sensitive to heat, and reductions at higher than room temperature result in the formation of products containing high percentages of arsenic. Most of the reductions were carried out at low temperatures.

When phenylglycine-*p*-arsonic acid or 3-amino-4-hydroxyphenylarsonic acid is reduced with β-hydroxyethylarsonic acid, the tetra-arseno compounds result rather than the arseno. This is due to the fact that these acids are very sensitive under the existing conditions, and apparently arsenic is split off in some manner from organic combination. This inorganic arsenic is then reduced simultaneously with the undecomposed acids, resulting in the formation of the tetra-arseno-ethanols. When 4-acetoxyphenylarsonic acid is reduced with β-hydroxyethylarsonic acid, the first product which separates is one which analyzes for three arsenic atoms in the molecule. The formation of this compound is no doubt similar to the formation of the tetra-arseno compounds.

Additional information as to the structure of these arseno compounds is gained from the fact that in alkaline solution they may be oxidized back to the arsonic acids and these acids may be recovered quantitatively. In the case of the arseno compounds from 4-hydroxyphenylarsonic acid and 4-acetoxyphenylarsonic acid, this oxidation was successfully carried out by means of hydrogen peroxide.

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[3] English patent 191,028 (1923); Quick and Adams, THIS JOURNAL, 44, 809 (1922).

All of the arseno-ethanols are finely divided, orange-yellow powders, the higher arseno compounds being darker colored. None can be crystallized and all are found to be completely soluble in reagents exerting a solubilizing influence upon the particular group present in the aromatic portion of the molecule.

Experimental Part

β-Hydroxyethylarsonic Acid, $H_2O_3AsCH_2CH_2OH$.—One-half mole (100 g.) of arsenic trioxide was dissolved in a solution of three moles (120 g.) of sodium hydroxide in 300 cc. of water. This was sufficient alkali to give the trisodium salt of arsenious acid. The mixture was cooled to room temperature and 1 mole (80 g.) of ethylene chlorohydrin was added dropwise during a period of thirty-five minutes. Vigorous stirring was employed during the whole operation and at the end of the addition the reaction mixture had become quite hot. The solution was allowed to stand overnight at room temperature, and was maintained, with stirring, at 80–90° on a hot water-bath for one hour.

At the end of this time the solution was cooled to 20° and glacial acetic acid was added until the solution reacted acid to litmus, about 65 cc. being required. The mixture was again cooled and the precipitated arsenious oxide was filtered off by suction and washed with 100 cc. of water. The filtrate was made strongly alkaline with ammonium hydroxide and any unreacted arsenious oxide remaining in solution was removed in the following manner. Hydrogen peroxide (3% solution) was added to the alkaline filtrate until the solution liberated iodine from potassium iodide solution. This was an indication that all of the trivalent arsenic had been oxidized by the peroxide solution to the pentavalent state and that the hydrogen peroxide was present in excess. In all about 210 cc. of the peroxide solution was added. The pentavalent arsenic was then precipitated as magnesium ammonium arsenate by the addition of an excess (about 500 cc. in all) of magnesia mixture. After standing overnight the precipitate was filtered off, the filtrate acidified with hydrochloric acid and evaporated on a steam-bath. The inorganic salts which separated were filtered off from time to time.

Absolute alcohol was then added to precipitate more of the inorganic salts and the filtered solution was again evaporated. After several such treatments the acid remained as a yellow oil. Ignition tests showed that no inorganic material was present and direct titration with iodine solution showed the absence of inorganic arsenic. An analysis of the oil made to determine the percentage which could be considered to be pure β-hydroxyethylarsonic acid showed it to be an 84.3% solution of the acid. The only impurities present were water and alcohol. After the acid had stood for a little over a year in a vacuum desiccator over sulfuric acid, it crystallized in large plates which contained one molecule of water of crystallization. This water was completely removed by heating in a vacuum drier at 80°. The anhydrous acid was found to be very hygroscopic and as a result a definite melting point could not be obtained. The compound melted between 157 and 159°.

Anal. Subs., 0.1035, 0.1041: 24.20, 24.35 cc. of I_2 soln. (1 cc. = 0.001884 g. As). Calcd. for $C_2H_7O_4As$: As, 44.11. Found: 44.05, 44.06.

Aryl Arseno-ethanols

4-Hydroxyphenylarseno-ethanol, $(HO)C_6H_4As{=}AsCH_2CH_2OH$.—To a solution of 6.44 g. of a 53% solution of β-hydroxyethylarsonic acid and 4.36 g. of 4-hydroxyphenylarsonic acid in 30 cc. of water and 10 cc. of hydrochloric acid (sp. gr., 1.19), 53 cc. of 50% hypophosphorous acid was added. The mixture was filtered and then placed in an ice-box. The color of the solution changed from a light yellow through orange to red.

At the end of two days an orange precipitate had separated. This was filtered off with suction, washed with dilute hydrochloric acid and water and dried in a vacuum over phosphorus pentoxide. Analysis and solubility tests showed that the compound was not quite pure, and so it was triturated for a short time with fresh portions of warm, dilute (1 to 5) hydrochloric acid. After this treatment the compound analyzed correctly for the unsymmetrical derivative. 4-Hydroxyphenylarseno-ethanol is an orange powder which is completely soluble in dilute aqueous alkalies; yield. 3.86 g., or 67%.

Anal. Subs., 0.1013, 0.1011: 34.60, 34.35 cc. of I_2 soln. (1 cc. = 0.001537 g. of As). Calcd. for $C_8H_{10}O_2As_2$: As, 52.08. Found: 52.49, 52.22.

The above product was further identified by the following experiment wherein the arseno compound was oxidized and the 4-hydroxyphenylarsonic acid recovered. Two grams of the arseno compound was put into solution in about 8 cc. of 12 *N* sodium hydroxide. The solution was warmed with stirring on a water-bath at 50°, and 5% hydrogen peroxide was added to it until all color disappeared. The mixture was stirred and maintained at this temperature for one and one-half hours. The solution was cooled under running water and hydrochloric acid (sp. gr., 1.19) was added until the reaction was acid to congo red. From this acid solution the 4-hydroxyphenylarsonic acid separated. The β-hydroxyethylarsonic acid, being water soluble, remained in solution. Two grams of $C_8H_{10}O_2As_2$ gave 1.501 g. of $C_6H_7AsO_4$; theoretical, 1.513 g.

4-Aminophenylarseno-ethanol Hydrochloride, $(H_2N)C_6H_4As{=}AsCH_2CH_2OH \cdot HCl$.—To a solution of 4.34 g. of arsanilic acid, 4.03 g. of an 84% solution of β-hydroxyethylarsonic acid in 10 cc. of hydrochloric acid (sp. gr., 1.19) and 10 cc. of water. 30 cc. of pyridine and 53 cc. of 50% hypophosphorous acid were added. The mixture was allowed to stand at ice-box temperature for three days. At the end of this time 200 cc. of hydrochloric acid (sp. gr., 1.19) was added and the mixture was again placed in the ice-box overnight. A copious orange-yellow precipitate formed which was filtered off by suction and washed with dilute hydrochloric acid and water. It was dried in a carbon dioxide filled desiccator over phosphorus pentoxide. An analysis of the compound showed that it contained 46.10% of arsenic and 10.49% of chlorine. The theoretical percentages in 4-aminophenylarseno-ethanol hydrochloride are 46.43 and 10.83, respectively. This, then, is the hydrochloride of the unsymmetrical compound.

In order to see the effect of water on this hydrochloride, the orange-yellow powder was triturated with warm water containing only the slightest trace of hydrochloric acid to prevent gumming. Analysis of the filtered and dried compound showed it to be the free base of 4-aminophenylarseno-ethanol.

This reduction was repeated with the exception that the pyridine was omitted. After fourteen days an orange-colored product weighing 1.20 g. had separated. This was filtered off, washed and dried in a vacuum over phosphorus pentoxide. When perfectly dry the compound was completely soluble in warm hydrochloric acid. A sodium fusion showed the absence of halogen. Analysis proved that this was the free base of 4-aminophenylarseno-ethanol, and the compound was identical in every respect with the free base obtained above.

Anal. Subs., 0.1005, 0.1005: 25.20, 25.20 cc. of I_2 soln. (1 cc. = 0.002083 g. of As). Calcd. for $C_8H_{11}ONAs_2$: As, 52.26. Found: 52.23, 52.23. Subs., 0.2014, 0.1963: 6.91, 6.71 cc. of 0.1 *N* HCl. Calcd. for $C_8H_{11}ONAs_2$: N, 4.87. Found: 4.79, 4.82.

Reduction of 4-Arsonophenoxyacetic Acid and β-Hydroxyethylarsonic Acid.—In an attempt to prepare 4-acetoxyphenylarseno-ethanol, 5.52 g. of 4-arsonophenoxyacetic acid and 4.03 g. of an 84% solution of β-hydroxyethylarsonic acid were dissolved in 30 cc. of water and 10 cc. of hydrochloric acid (sp. gr., 1.19). To this was added 53 cc. of 50% hypophosphorous acid and the filtered solution was placed in an ice-box.

After three days there was no evidence of reduction and so the flask and its contents were warmed to 60° for ten minutes. The solution immediately became cloudy and turned a light yellow color. A yellow, alkali soluble precipitate weighing 1.33 g. separated. This was filtered off, washed with dilute hydrochloric acid and water and dried *in vacuo* over sulfuric acid.

Anal. Subs., 0.1020, 0.0984: 26.20, 25.10 cc. of I_2 soln. (1 cc. = 0.002083 g. of As). Calcd. for $C_{10}H_{12}O_4As_3$: As, 53.40. Found: 53.50, 53.15.

An oxidation of 0.8234 g. of this compound gave 0.522 g. of 4-acetoxyphenylarsonic acid; theoretical, 0.539 g. It is probable, then, that this compound is the unsymmetrical triarseno-ethanol.

In order to prepare the arseno compound, the reduction was repeated using the same amounts of the respective arsonic acids and the same amounts of hydrochloric and hypophosphorous acids. The procedure was varied, however, in that the reduction mixture was allowed to stand at room temperature (without heating) for ten days. At the end of that time a yellow, alkali-soluble precipitate similar to the one obtained above had separated. The analysis showed that this was 4-acetoxyphenylarseno-ethanol; yield, 2.34 g., or 36%.

Anal. Subs., 0.1002, 0.1009: 21.30, 21.40 cc. of I_2 soln. (1 cc. = 0.002083 g. of As). Calcd. for $C_{10}H_{12}O_4As_2$: As, 44.62. Found: 44.23, 44.17.

The above compound was further identified by oxidation with hydrogen peroxide and recovery of the 4-acetoxyphenylarsonic acid; 1.5413 g. of $C_{10}H_{12}O_4As_2$ gave 1.228 g. of $C_8H_9O_6As$; theoretical, 1.230 g.

3-Amino-4-hydroxyphenyl-tetra-arseno-ethol, $3\text{-}(H_2N)\text{-}4\text{-}(HO)C_6H_3As{=}As{-}As{=}As{-}CH_2CH_2OH$.—A solution of 4.66 g. of 3-amino-4-hydroxyphenylarsonic acid and 3.76 g. of β-hydroxyethylarsonic acid monohydrate was made in 15 cc. of water and 15 cc. of hydrochloric acid (sp. gr., 1.19). To this was added 53 cc. of 50% hypophosphorous acid and the mixture was allowed to stand at a temperature of 15° for six days. The orange product which formed was filtered off by suction, washed well with dilute hydrochloric acid and water and dried over phosphorous pentoxide. A sodium fusion showed the absence of halogen. The compound was soluble in dilute aqueous alkalies, and concentrated hydrochloric acid; yield, 1.02 g., or 11.2%.

Anal. Subs., 0.1000, 0.1000: 57.50, 67.55 cc. of I_2 soln. (1 cc. = 0.001208 g. of As). Calcd. for $C_8H_{11}O_2NAs_4$: As, 69.93. Found: 69.46, 69.52. Subs., 0.1297, 0.2041: 28.18, 44.64 cc. of 0.01 N HCl. Calcd. for $C_8H_{11}O_2NAs_4$: N, 3.09. Pound: 3.04, 3.05.

The reduction was repeated in an attempt to prepare the arseno compound. In the second reduction the conditions were the same as in the above with the exception that the reduction mixture was diluted with distilled water to a total volume of 450 cc. The orange product which separated was in all respects identical with the one described above.

4-Glycinephenyl-tetra-arseno-ethanol, $(HOOCCH_2NH)C_6H_4As{=}As{-}As{=}As{-}CH_2CH_2OH$.—A solution of 5.5 g. of phenylglycine-*p*-arsonic acid and 3.76 g. of β-hydroxyethylarsonic acid monohydrate was made in 15 cc. of water and 10 cc. of hydrochloric acid (sp. gr., 1.19). In order to insure complete solution, the mixture was warmed gently. After the solution had cooled, it was filtered and 53 cc. of 50% hypophosphorous acid was added. The reduction mixture was allowed to stand at an average temperature of 10°. After two days 1.268 g. of a finely-divided orange precipitate separated. This was completely soluble in dilute aqueous alkalies.

Analysis showed it to be the tetra-arseno compound.

Anal. Subs., 0.1000, 0.1000: 50.00, 50.00 cc. of I_2 soln. (1 cc. = 0.01199 g. of As). Calcd. for $C_{10}H_{13}O_3NAs_4$: As, 60.60. Pound: 59.95, 59.95. Subs., 0.1210, 0.1512:

23.78, 30.04 cc. of 0.01 *N* HCl. Calcd. for $C_{10}H_{13}O_3NAs_4$: N, 2.82. Found: 2.75, 2.78.

Summary

1. β-Hydroxyethylarsonic acid has been obtained in a crystalline form.
2. A series of aryl arseno-ethanols has been prepared by the simultaneous reduction of β-hydroxyethylarsonic acid and various aromatic arsonic acids.
3. One member of the previously unknown series of unsymmetrical aliphatic-aromatic tri-arseno compounds has been made.

SAINT PAUL, MINNESOTA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF HEMOCYANIN

BY THE SVEDBERG AND EUGEN CHIRNOAGA[1]

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Hemocyanin is the respiratory blue pigment of the blood of certain lower animals: molusca, crustacea and arachnoides.[2,3,4] Both in physiological function and in composition it shows a certain analogy to hemoglobin, the respiratory pigment of the blood of higher animals. The hemocyanin molecule has a metallic constituent, copper, while hemoglobin contains iron. Hemocyanins from different species seem to differ in their copper content. Griffiths[5] found for *Cancer, Homarus* and *Sepia* about 0.33%; Heinze[6] for *Octopus vulgaris* 0.38%; Burdel[7] and Begemann[8] for *Helix pomatia* about 0.27%; Alsberg and Clark[9] for *Limulus polyphemus* 0.28%; while Redfield, Coolidge and Shotts[10] in a very careful investigation found for the same species 0.173%. The differences in the copper content as well as in other properties, for example, the oxygen combining curve, seem to indicate that there exist different kinds of hemocyanin.

Because of the physiological importance of hemocyanin it was thought to be of interest to study its actual molecular weight in solution by means of the new method of ultracentrifuging, already applied to the study of hemoglobin, egg albumin, phycoerythrin and phycocyan.

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[1] Fellow of the International Education Board.

[2] Frédéricque, *Arch. Zoöl.*, 7, 535 (1878).

[3] Ch. Dhéré, *Arch. de Physiol. et Pathol. gen.*, 16, 985 (1916); 18, 221 (1919).

[4] J. Botazzi, *ibid.*, 18, 1 (1919).

[5] Griffiths, *Compt. rend.*, 114, 496 (1892).

[6] Heinze, *Z. physiol. Chem.*, 33, 370 (1901); 43, 290 (1904).

[7] Burdel, *Thèses*, Fribourg, 1922.

[8] Begemann, *Proefschrift*, Utrecht, 1924.

[9] Alsberg and Clark, *J. Biol. Chem.*, 8, 1 (1910).

[10] Redfield, Coolidge and Shotts, *ibid.*, 76, 185 (1928).

This paper deals with hemocyanin extracted from the blood of the vineyard snail, ***Helix pomatia***.

Experimental

Preparation of Material.—Nine hundred cc. of blood was obtained from **800** hibernating snails. The shells were cut into opposite the heart, recognized by its blue color. The heart was pierced by a needle and the blood allowed to drop into a crucible.[11] The freezing point depression of fresh blood was 0.45°.

For the isolation of hemocyanin the blood was transferred to collodion bags and put to dialyze in a box kept at 0°, according to the procedure followed by Dhéré.[12] The distilled water flowing into the vessel containing the collodion bags was kept saturated with toluene in order to prevent the growth of bacteria. After two weeks a voluminous precipitate was deposited in each bag, leaving a slightly blue supernatant liquid. After centrifuging, the precipitate dissolved readily in dilute solutions of sodium chloride, sodium phosphate, acetic acid and other electrolytes. A second dialysis was continued until the conductivity of the liquid had fallen at room temperature to 6.1×10^{-6} mhos.

Under the microscope the deposit showed numerous crystals, most of them forming crosses, five and six branched stars and several clearly revealed the octahedral shape. Fig. 1 shows dendrite crystals from a solution dialyzed against distilled water. Fig. 2 reproduces individual crystals precipitated by electrodialysis from a dilute solution which would no longer give any deposit even after prolonged ordinary dialysis. Good photographs were obtained with difficulty because hemocyanin is extremely sensitive to alkali, dissolving in contact with the glass of the microscopic slide. Well shaped crystals maintain their form only for a short period of time, shrinking on drying. This suggests that they are of a semi-liquid nature. Unlike Dhéré we did not use alcohol or fuchsine in photographing our crystals, thereby avoiding the possibility of producing denaturation of the protein.

It may be added that electrodialysis produces total deposition of hemocyanin from its solutions in less than twenty-four hours, while the conductivity of the liquid drops to that of distilled water. If the solution has been very dilute the precipitate will dissolve again through the action of the alkali of the glass on breaking the current and shaking.

The ultramicroscope reveals no discrete particles in a solution of hemocyanin, but the cone of light can be seen distinctly even at a dilution of 0.0001%.

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[11] We wish to express our thanks to Dr. S. Bock for his kind assistance in procuring the snails and for his kind advice as to the best way of drawing their blood.

[12] Ch. Dhéré, *Thèses*, Fribourg, 1909.

The precipitate obtained after dialyzing the blood three times down to a specific conductivity of 6×10^{-6} mhos was used for making up the solutions of different PH for the following measurements.

The isoelectric point was assumed to be at PH 4.7 as stated by Quagliariello[13] for hemocyanin from Octopus. After the completion of the present investigation, the isoelectric point of our hemocyanin material was determined in this Laboratory by A. Tiselius. He found by means of cataphoresis measurements *P*H 5.2.[14]

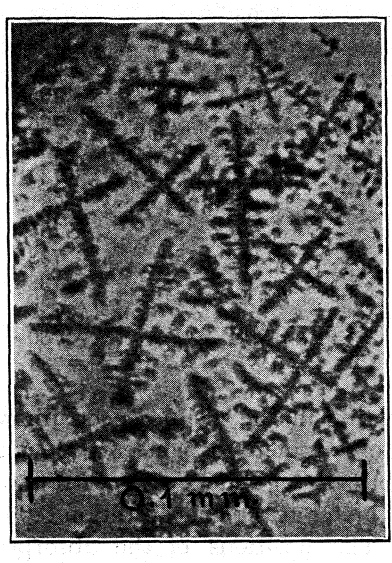

Fig. 1.

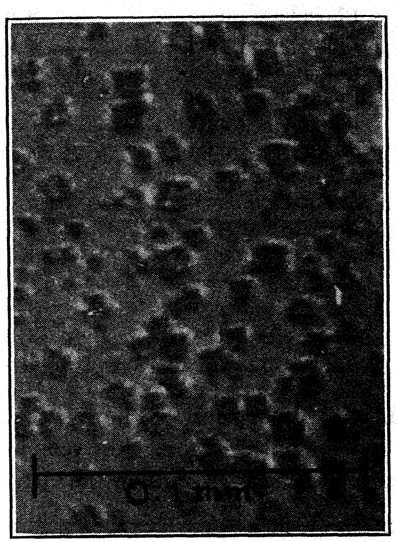

Fig. 2.

Specific Volume.—The partial specific volume of hemocyanin was determined pycnometrically at 19.5° and calculated according to the formula $V = [w - (l - h)]/\rho h$, where V is the partial specific volume, w the weight of solvent in the pycnometer, l the weight of solution, h the weight of the protein and ρ the density of solvent.

The concentration of the solutions was determined by transferring one cc. of solution to a porcelain crucible, evaporating down to coagulation on a water-bath and then drying to constant weight at 105°. From the weight so found, the content of salt in one cc. of solution was subtracted. Another method employed was to coagulate at 82–83° one cc. of solution in a small flask, wash with boiled water and dry to constant weight as

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[13] Quagliariello, *Atti acad. med. chir. Napoli*, 74 (1920); *Die Naturwissensch.*, 11, 261 (1923).

[14] The Referee has kindly drawn our attention to a recent paper by E. and E. Stedman, Biochem. J., 21, 533 (1927), where the isoelectric point of hemocyanin from *Helix pomatia* is given as PH 5.3.

before. The results obtained by the two methods agree very well. The figures for the partial specific volume of the protein in solutions at various PH and concentrations are given in Table I. Except in alkaline solutions, PH 8, the partial specific volume is practically independent of *P*H.

TABLE I

PARTIAL SPECIFIC VOLUME FOR HEMOCYANIN FROM *Helix pomatia*

Solvent	*P*H	Concentration, %	V
Phosphate buffer	8.0	6.10	0.755
Phosphate buffer	8.0	3.05	.753
Phosphate buffer	8.0	1.53	.754
Phosphate buffer	7.0	9.40	.735
Phosphate buffer	7.0	4.70	.735
Phosphate buffer	7.0	2.35	.736
Phosphate buffer	7.0	1.18	.737
Acetate buffer	5.6	3.38	.732
Acetate buffer	5.6	1.69	.731
Acetate buffer	4.7	5.29	.735
Acetate buffer	4.7	2.64	.738
Acetate buffer	4.7	1.32	.738
Acetate buffer	3.8	3.47	.733
Acetate buffer	3.8	1.74	.730
Acetate buffer	3.8	0.87	.733

Light Absorption.—The light absorption in the visible spectrum was measured with a Konig-Martens spectrophotometer at concentrations between 1.2 and 1.7% and in the ultraviolet with a Judd-Lewis spectrophotometer at the concentration 0.05%. The positions of the absorption maxima agree with those found by Dhéré and Burdel.[12,15] In the visible spectrum we found an absorption band between 610 and 530μμ; in the ultraviolet there is a first absorption band between 360 and 310μμ and a second one much more pronounced between 290 and 260μμ, with a maximum at 278μμ. Table II gives the values of the extinction coefficients per unitconcentration, $\epsilon/c = 1/dc \cdot \log I/I_0$, for solutions of PH 3.8, 4.7, 5.6, 7.0 and 8.0 in the visible spectrum.

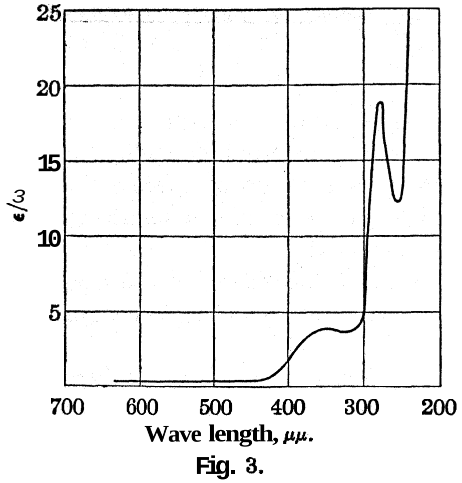

Fig. 3.

The extinction coefficient cannot be measured with great accuracy in the Judd-Lewis spectrophotometer and for this reason the figures for

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[15] Ch. Dhéré and A. Burdel, *Journ. de Physiol. et Pathol.* gen., 18, 685 (1919-20).

the ultraviolet are not tabulated. The whole absorption curve in the visible and the ultraviolet spectrum for a solution of Pн 4.7 and one weight per cent. concentration is given in Fig. **3.** In order to bring out more clearly the maximum in the visible spectrum, part of the curve, from 650 to 400μμ, is reproduced in larger scale in Fig. 4.

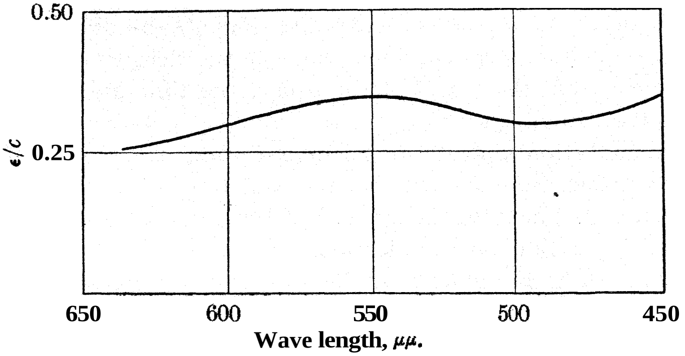

Fig. 4.

TABLE II

LIGHT ABSORPTION FOR HEMOCYANIN FROM *Helix pomatia*

ϵ/c

Wave length, μμ	Pн 3.8, 1.75%	*P*н 4.7, 1.32%	Pн 56, 1.69%	Pн 7.0, 1.17%	*P*н 8.0, 1.52%
635	0.199	0.253	0.297	0.262	0.267
605	.229	.294	.339	.308	.304
579	.248	.325	.377	.335	.329
556	.249	.345	.395	346	.343
538	.238	.341	.401	.344	.352
522	.216	.341	.396	.346	.336
506	.206	...	.361	.347	.341
492	.200	.299	.360	,377	.375
479	...	...	.349	...	.317
468	.197	...	.346	...	.322

The light absorption varies slightly with the age of the solution, though the general shape of the curve remains exactly the same. Since our solutions were of different ages, from one day to several weeks, no weight should be put on the small variation of ϵ/c with *P*н as shown in Table II within the region Pн 4.7 to 8.0. At the acid side of the isoelectric point, however, the absorption in the visible spectrum is decidedly lower and the maximum seems to be slightly shifted toward the red. As demonstrated by the centrifuging experiments, the huge hemocyanin molecule which exists in solution at and above the isoelectric point is broken up into smaller units at Pн **3.8** and the decrease in light absorption is probably a consequence of this disintegration.

Determination of the Molecular Weight

A. Sedimentation Velocity **Method.**[16,17]—The molecular weight is given by

$$M = \frac{RT\,s}{D(1 - V\rho)}$$

where R is the gas constant, T the absolute temperature, s the specific sedimentation velocity defined as $[dx/dt \cdot 1/\omega^2 x]$, D the diffusion constant of the solute, V its partial specific volume, ρ the density of the solution, x the distance from the center of rotation, t the time and ω the angular velocity of the centrifuge.

l'he sedimentation velocity is calculated from the movement of the boundary between, pure solvent and solution towards the periphery and the diffusion constant from the amount of blurring of the same boundary as described in previous communications.

In order to make the values from different runs comparable, the specific sedimentation velocities were all reduced to 20° by means of the relation $s_1/s_2 = \eta_2/\eta_1$, and the diffusion constants by means of the relation $D_1/D_2 = T_1\eta_2/T_2\eta_1$, where η is the viscosity of the solution. Variations in the intensity of the lamp were corrected for by using a standard solution of potassium chromate of suitable strength. In the earlier runs Hauff Ultra Rapid plates were used; later it was found that Imperial Process plates gave better results.

The changes in concentration taking place in the solution enclosed in the centrifuge cell could not be followed photographically in the visible light absorption band $570\mu\mu$ on account of the small absorption and therefore in the first series of experiments long wave ultraviolet light ($366\mu\mu$) was used corresponding to the absorption maximum at $360\mu\mu$. This light was isolated from the other radiations of the mercury lamp by means of a nickel glass filter.

Our first run was made with a solution of PH 8.0 and concentration 3.05% at a speed of 7000 r.p.m. (centrifugal force 2565 times that of gravity). It was found that the sedimentation equilibrium expected in analogy to the behavior of the other proteins previously investigated was not attained. Instead the molecules were centrifuged down, leaving a sharp boundary between solution and solvent. Three successive experiments were carried out with the above solution at speeds of 4000, 8000 and 11,000 r.p.m., all other conditions being equal, The obtained values for the diffusion constant indicated a variation approximately inversely proportional to the centrifugal force applied. At the same time it was noticed that during centrifuging some change took place in the solution, starting from the bottom of the cell, causing less light

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[16] Svedberg, *Z. physik. Chem.*, 127, 51 (1927).

[17] Svedberg and Nichols, THIS JOURNAL, 49, 2920 (1927).

absorption and consequently undue darkening of the photographs in the affected region. This darkening extended rapidly upwards, altering the blurring of the boundary and therefore preventing accurate calculation of the diffusion constant. The effect was more marked with old than with fresh solutions. It was assumed to be due to reduction of the hemocyanin produced by the activity of bacteria present in the solutions since the medium was alkaline.[18,19]

A few experiments carried out at PH 3.8 indicated a breaking up of the molecule into smaller units of varying size. Because of the instability of the protein both in alkaline and extremely acid solutions, we decided to limit the present investigation of the molecular weight to solutions near the isoelectric point, which offered better conditions of stability.[20]

Long wave ultraviolet light was used down to a concentration of 0.68%. Several experiments made at this point could not be calculated on account of insufficient contrast in the photographs between solution and solvent and therefore we passed over to short ultraviolet light isolated from the radiation of the mercury arc by means of chlorine and bromine filters. Even in this case at a dilution of 0.1% the cell of 2 mm. thickness used in previous investigations had to be replaced by one 8 mm. thick in order to have sufficiently strong absorption to permit the taking of suitable photographs.

Our data obtained by ultracentrifuging of hemocyanin solutions at PH 4.7 soon brought to light the strange phenomenon of a strong variation of the diffusion "constant" with concentration of the protein solution.

TABLE III

SEDIMENTATION VELOCITY AND DIFFUSION FOR HEMOCYANIN FROM *Helix pomatia*

Concentration, 3.05%; *PH*, 8.0 (phosphate buffer); $V = 0.753$; $T = 291.5$; length of column of solution, 0.99 cm.; thickness of column, 0.20 cm.; speed, 11,000 r.p.m. ($\omega = 366.7\pi$); time of exposure, 20 secs.

Time interval, min.	Δx cm. per 30 min.	x, mean cm.	$s_{20°}$, cm./sec.	$D_{20°}$, cm.^{2}/day
30–60	0.054	3.796	5.79×10^{-12}	1.48×10^{-3}
60–90	.063	3.854	6.80	0.99
90–120	.058	3.914	6.11	1.31
120–150	.062	3.974	6.44	0.95
150–181	.065	4.039	6.69	1.05
181–219	.060	4.111	6.08	1.41
219–248	.066	4.182	6.47	1.24
		Mean	6.34×10^{-12}	1.20×10^{-3}

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[18] Alsberg, J. *Biol.* Chem., 23, 495 (1915).

[19] Phisalix, *Compt. rend. soc. biol.*, 52, 729 (1900).

[20] For the isoelectric point we had accepted Quagliariello's value, *PH* 4.7. As stated above the isoelectric point of the material used was actually *PH* 5.2. An investigation on the stability region of the same hemocyanin material carried out in this Laboratory by F. F. Heyroth has shown that there is no change in molecular weight between PH 4.7 and 5.2.

TABLE IV

SEDIMENTATION VELOCITY AND DIFFUSION FOR HEMOCYANIN FROM *Helix pomatia*

Concentration, 0.17%; PH 4.7 (acetate buffer, 0.02 N with regard to Na); V = 0.738; T = 291.8; length of column of solution, 0.95 cm.; thickness of column, 0.80 cm.; speed, 11,000 r.p.m. (w = 366.7 π); time of exposure, 40 secs.

Time interval, min.	Ax, cm. per 30 min.	x, mean cm.	$s_{20°}$ cm./sec.	$D_{20°}$, cm.²/day
60– 90	0.089	3.897	9.56×10^{-12}	11.0×10^{-3}
90–120	.095	3.989	9.91	16.1
120–150	.098	4.085	9.77	17.3
150–180	.104	4.186	10.30	14.8
180–210	.095	4.286	9.16	15.2
210–240	.105	4.386	10.20	15.5
		Mean	9.8×10^{-12}	15.0×10^{-3}

M = 4.93×10^{6}

This fact had not been met with in the study of the other proteins investigated by this method. However, the change in the values of D with the centrifugal force observed at PH 8 was no longer encountered with isoelectric solutions.

Details of two typical runs under widely different conditions are given in Tables III and IV.

In Table V all the determinations of diffusion constant and specific

TABLE V

SEDIMENTATION VELOCITY AND DIFFUSION FOR HEMOCYANIN FROM *Helix pomatia*

Concn., %	PH	R.p.m.	$D_{20°} \times 10^{3}$, cm.²/sec.	$s_{20°} \times 10^{12}$, cm./sec.
3.05	8.0	4000	3.82	5.63
3.05	8.0	8000	2.34	6.57
3.05	8.0	11000	1.47	6.80
3.05	8.0	11000	1.38	6.37
2.60	4.7	4000	4.50	...
2.60	4.7	11000	4.70	8.15
1.36	4.7	3000	7.67	...
1.36	4.7	4000	9.55	8.80
0.68	4.7	4000	9.50	8.60
0.68	4.7	6000	8.73	8.96
0.34	4.7	6000	14.5	9.30
0.34	4.7	4000	12.0	9.30
0.34	4.7	4000	10.2	9.25
0.34	4.7	8000	13.0	8.94
0.17	4.7	4000	11.0	9.05
0.17	4.7	8000	14.6	9.70
0.17	4.7	8000	12.3	9.60
0.17	4.7	11000	15.3	9.80
0.074	4.7	4000	14.0	8.55
.074	4.7	6000	15.1	9.90
.074	4.7	8000	15.6	10.3
.051	4.7	6000	16.5	...
.049	4.7	10000	16.0	...

sedimentation velocity are given. Fig. 5 demonstrates the variation of diffusion constant and sedimentation velocity with concentration at a P_H of 4.7. Both the table and the curve show that at a concentration of 0.1% and below, the values of D remain independent of concentration, indicating that we have reached a region of normal diffusion conditions. The values of s also show a slight variation with concentration. This change, however, is not at all comparable to that of the diffusion constant.

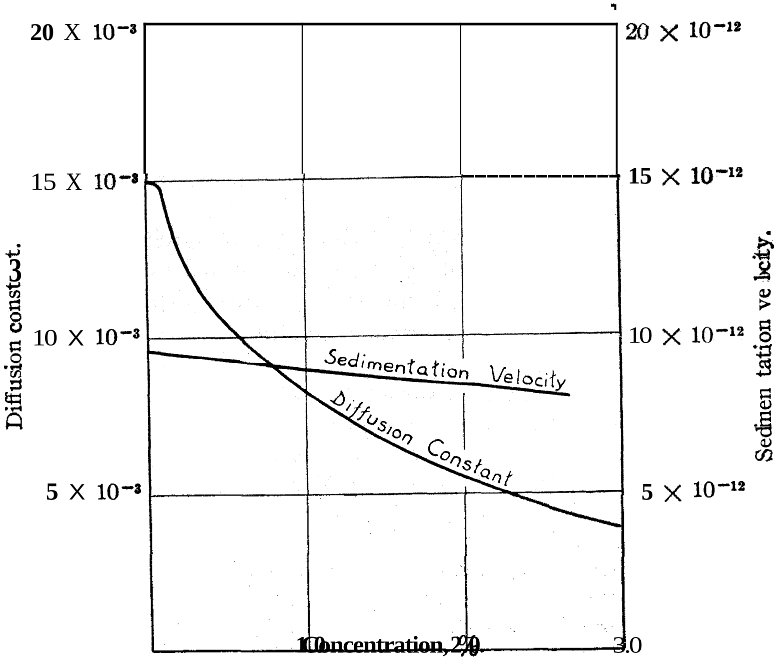

Fig. 5.

Taking for D the mean value 15.4×10^{-3} from the five determinations below 0.1% and for s the mean value 9.42×10^{-12} from the 11 determinations below 0.4%, we get for the molecular weight 4.93×10^6.

B. Sedimentation Equilibrium **Method.**[21,22,23]—The molecular weight is given by

$$M = \frac{2RT \ln(c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where R, T, V, ρ and ω have their usual meaning and c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation.

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[21] Svedberg and Fåhraeus, THIS JOURNAL, 48, 430 (1926).

[22] Svedberg, *Z. physik. Chem.*, 121, 65 (1926).

[23] Svedberg and Nichols, THIS JOURNAL, 48, 3081 (1926).

This method is based on the equilibrium reached in the cell during centrifuging between diffusion and centrifugal force and may only be applied when the conditions insure normal diffusion. It was found by the sedimentation velocity method that in the case of hemocyanin it is essential to study only very dilute solutions, less than 0.1% in weight. Because of the enormous molecular weight only a very low centrifugal force was permissible. Even at a speed of only 3000 r.p.m. no equilibrium could be obtained but the solute molecules and the solvent separated clearly. Therefore speeds of about 1000 r.p.m., giving a centrifugal force only 50–60 times greater than gravity, were used in the following experiments. With columns of solution not longer than 3 4 mm., equilibrium was attained after two to three days of centrifuging.

Standard solution and plates were the same as for the sedimentation velocity runs.

Details of a typical run are given in Table VI. In Table VII a summary of results from eight experiments is given, all carried out with solutions of P_H 4.7 and at concentrations below 0.09%; three exposures were used for the calculation of each molecular weight value.

TABLE VI

SEDIMENTATION EQUILIBRIUM OF HEMOCYANIN FROM *Helix pomatia*

Concentration, 0.051%; P_H = 4.7; length of column of solution, 0.315 cm.; thickness of column, 0.80 cm.; distance of the bottom of the cell from axis of rotation, 4.73 cm.; T = 288.3; speed, 1180 r.p.m. ($w = 39.3\,n$).

Distances, cm.		Mean concn., %		
x_2	x_1	c_2	c_1	M
4.720	4.685	0.0683	0.0548	5.64×10^6
4.685	4.635	0.0548	0.0448	5.20
4.635	4.585	0.0448	0.0377	4.51
4.585	4.535	0.0377	0.0312	4.99
4.535	4.485	0.0312	0.0260	4.87
4.485	4.435	0.0260	0.0214	5.25
			Mean	5.08×10^6

TABLE VII

MOLECULAR WEIGHT OF HEMOCYANIN FROM *Helix pomatia*

Concn., %	Length of column of solution, cm.	M
0.082	0.37	5.05×10^6
.082	.39	5.22
.074	.39	4.84
.074	.46	4.79
.051	.32	5.07
.051	.38	5.06
.049	.30	5.24
.049	.33	5.15
	Mean	5.08×10^6

Discussion of Results

All the experimental evidence reviewed in this paper indicates five million as the most probable value for the actual molecular weight of hemocyanin from *Helix pomatia* in dilute solution near the isoelectric point. Assuming the molecules to be spherical, we obtain 12.0×10^{-7} cm. for its radius by means of Stokes' law, $r = \sqrt{9\eta s/2\Delta\rho}$, where η is the viscosity of the solution, s the specific sedimentation velocity and $\Delta\rho$ the difference in density between the protein molecule and the solvent. The density of the protein molecule was taken as the reciprocal of the partial specific volume experimentally determined. The radius may also be calculated from the Einstein formula, $r = RT/6\pi\eta ND$, where D is the diffusion constant and N the Avogadro constant. In this way we get $r = 12.2 \times 10^{-7}$ cm. The fact that these two values agree so closely indicates that the particle cannot deviate much from the spherical shape. This particle size is about at the limit of visibility in the ultramicroscope for metallic particles when illuminated with light from the carbon arc. However, particles of an organic substance can only be seen when much larger and therefore it is obvious that we cannot expect to make the molecule of hemocyanin visible in the ultramicroscope.

In order to ascertain whether the particles are of uniform size, we carried out an experiment at a speed of 25,000 r.p.m., corresponding to a centrifugal force 37,000 times greater than that of gravity, with a solution at P_H 4.7 and of concentration 0.051% at a temperature of 23°, taking photographs every three minutes, the whole experiment lasting only half an hour. During such a short interval of time no appreciable diffusion takes place, and if the solution contains molecules of the same size, the photographs must display a sharp boundary between solvent and solution. Fig. 6 shows that same photograph (upper picture) in comparison with a similar one (lower picture) taken during the centrifuging of a gold sol at five minute intervals and at a speed of 22,000 r.p.m. and a temperature of 28.5°.[24] The difference in their appearance is obvious. While the boundary formed by the centrifuged hemocyanin molecules is quite sharp, that in the gold sol is blurred and becomes more so as the particles travel further toward the bottom of the cell. The gold colloid used was prepared by reducing gold chloride by phosphorus and is known to be one of the most uniform synthetic colloids. The radius (determined by H. Rinde) ranges from 1.5–3.3$\mu\mu$, the maximum in the distribution curve being at 2.5$\mu\mu$.

The sharp boundary shown in the photograph, the constancy of the molecular weight determined at various distances from the center of rotation in the sedimentation equilibrium experiment (Table VI) and the constancy with time of the value of the diffusion constant obtained in

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[24] **Rinde, *Dissertation,* Upsala, 1928.**

the sedimentation velocity method (Table IV) all justify the conclusion that, notwithstanding their size and enormous weight, the hemocyanin particles are entitled to be considered as real molecules acting as single units.

The variation of diffusion "constant" with concentration noted in the sedimentation velocity measurements can be explained on the assumption that in concentrated solutions, probably on account of their unusual size, and therefore proximity, there are forces at work acting between the molecules, preventing a completely free movement, which results in a greater frictional force opposed to the diffusion. As the dilution increases and with it the distance between molecules, these intermolecular forces become weaker, until at a certain limit concentration they disappear and the molecules are completely free to move about. This is the state which we have previously termed normal diffusion conditions. It must be clearly understood that in our conception no compact groups of molecules are formed which would modify the total molecular surface. On this assumption it can be theoretically proved that the diffusion constant will change with the concentration of the solution, while the sedimentation velocity should not appreciably do so. A simple calculation shows that in a 3% solution of hemocyanin (the concentration present in the snail blood) the average distance between the surfaces of adjacent molecules is only about one and a half times the molecular diameter.

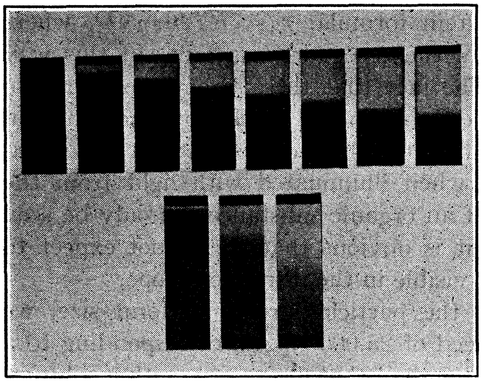

Fig. 6.

Summary

1. The centrifugal methods have been applied to the study of the molecular weight of hemocyanin from Helix *pomatia*.

2. The unexpected phenomenon of a strong variation of its diffusion constant with concentration down to a certain low limit of concentration has been encountered and an assumption has been put forward to explain it.

3. Both the sedimentation velocity and sedimentation equilibrium methods for determining the molecular weight have resulted in good agreement in the figure of 5,000,000 ± 5% as the most probable value in dilute solution at P_H 4.7.

4. Within the limits of experimental error all the molecules of a dilute solution of hemocyanin from Helix *pomatia* at P_H 4.7 are found to be of equal weight and size and this protein is therefore probably to be regarded as a chemical individual.

5. As to shape, the calculations based on our experimental data indicate that at P_H 4.7 the molecules are practically spherical with a radius of 12.1×10^{-7} cm.

UPSALA, SWEDEN

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XIII. PROPERTIES OF GAMMA-DELTA-DIHYDROXY-CARBONYL DERIVATIVES AND THEIR BEARING ON THE POLYMERIZATION OF POLYSACCHARIDES

BY HAROLD HIBBERT AND C. PAULINE BURT[1]

RECEIVED NOVEMBER 30, 1927 PUBLISHED MAY 5, 1928

In previous communications[2] the important role played by adjacent hydroxyl groups in the γ,δ-positions to the carbonyl group has been emphasized and evidence submitted of the tendency of such compounds to readily lose a molecule of water with subsequent formation of a highly polymerized product. The bearing of such phenomena on the problem of the constitution of cellulose and related compounds has been repeatedly indicated.[2]

Further evidence is now available in that a second dihydroxy carbonyl derivative, namely, methyl γ,δ-dihydroxy amyl ketone has been synthesized and found to show a similar behavior to that of the methyl γ,δ-dihydroxy butyl ketone previously investigated.[2c]

Thus in presence of a trace of concentrated sulfuric acid at about 90°, it readily loses a mole of water per mole of the ketone, yielding a viscous, resinous substance which is found to be a polymerized product having a molecular weight in benzene solution of 553–590.

The molecular weight of the corresponding product from methyl γ,δ-dihydroxy butyl ketone is shown to vary between 395 and 445 in phenol solution and to increase to 3706 when camphor is used as the solvent.

Assuming the methyl γ,δ-dihydroxy amyl ketone to possess the butylene oxide structure, the change may be represented as follows.

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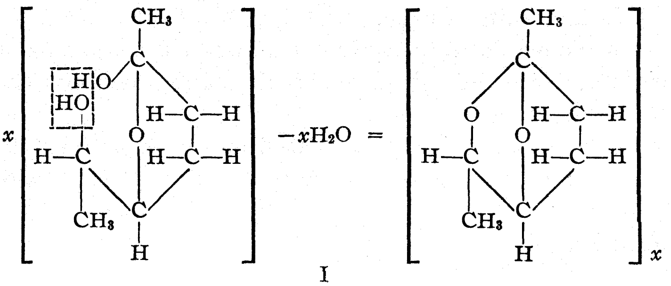
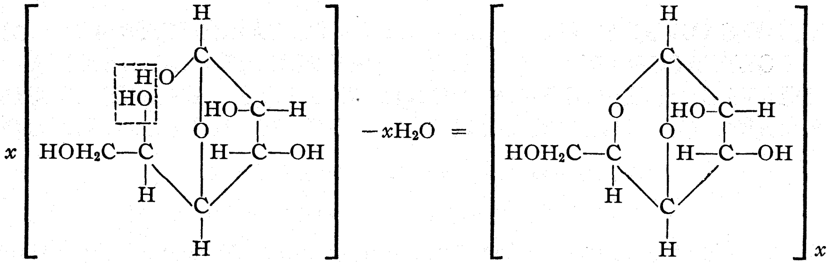
[1] Constructed from the dissertation presented by C. Pauline Burt to the Faculty of the Graduate School of Yale University, June, 1925, in candidacy for the degree of Doctor of Philosophy.

[2] (a) Hibbert, *Chem. Met. Eng.*, 22, 838 (1920); (b) *J. Ind. Eng. Chem.*, 13, 256, 334 (1920); (c) Hibbert and Timm, THIS JOURNAL, 45, 2433 (1923).



I

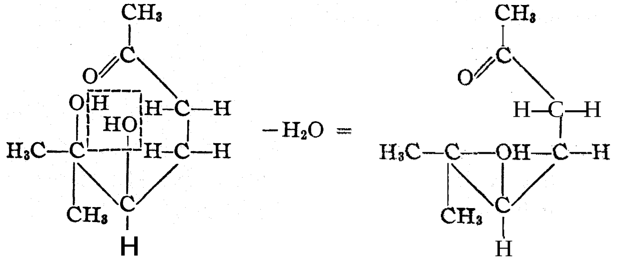
Its formation is thus probably analogous to the change taking place in the transformation of glucose into cellulose.[2a,b]



II Polymerized glucose anhydride

Whether the nucleus (cellulose) consists of one[3] or several[4] glucose anhydride units is at present unknown, as is also the nature of the forces (secondary valence, crystallographic, etc.)[5] which serve to hold the larger aggregate together.

On the other hand, the next higher homolog, methyl γ,δ-dihydroxy *iso*valeryl ketone, under the same conditions, readily loses a molecule



III

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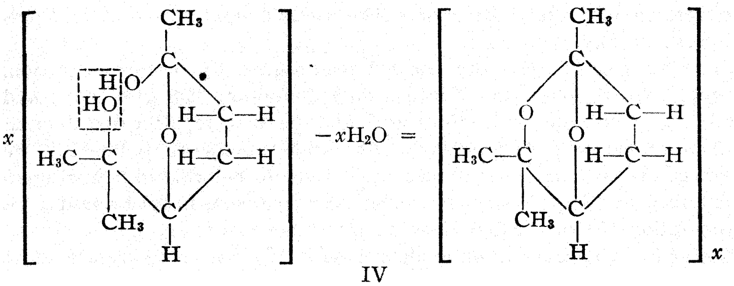
[3] Hess and Messmer, Ann., **435,** **7,** 111 (1923); Hess, Messmer and Ljubitsch, Ann., **444,** 287 (1925); Hess, Ann., **450,** 65 (1926); Pringsheim and co-workers, Ann., 448, 163 (1926).

[4] Hibbert, *loc. cit.;* Irvine, Brit. Assocn. Adv. *Sci.*, **1922,** p. 14; Karrer, "Die Polysaccharide," Akademische Verlagsgesellschaft, Leipzig, **1925,** pp. 217–240; Sehorger, Ind. *Eng. Chem.,* **16,** 1274 (1924); Gray, *Ind.* Eng. Chem., **18,** 811 (1926).

[5] For synopsis see "Handbuch der normalen und pathologischen Physiologie," Verdauung und Verdauungsapparat-Verlag, Julius Springer, Berlin, Vol. III, **1927,** pp. **922-924.**



IV

of water from the γ,δ-hydroxyl groups with formation of a 1:2 oxide, and exhibits practically no tendency toward a dehydration involving the carbonyl group; that is, Reaction III is favored rather than IV. The reason for this difference in behavior is, in all probability, to be found in the alteration in the valence angle of the carbon atom to which the two methyl groups are attached,[6] the latter producing a deviation favorable to the formation of a three-membered ring, but operating against a reaction between the ketohydrol and the y-hydroxyl group.[7]

Experimental

Synthesis of Methyl **γ,δ-Dihydroxy Amyl** Ketone ($CH_3CHOH\text{-}CHOH(CH_2)_2\text{-}COCH_3$).—This was prepared by the following synthetic reactions: crotonaldehyde → crotyl alcohol → crotyl bromide → crotyl ethyl aceto-acetate → Δ^{5-6} heptene-2-one → methyl γ,δ-dihydroxy amyl ketone.

Reduction of Crotonaldehyde to Crotyl Alcohol.—This was carried out by Charon's method[8] in acetic acid solution by means of the zinc-copper couple. The yield after purification (b. p. 116–118°) is small, the principal product being dipropenyl glycol.

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[6] Ingold, J. *Chem. Soc.*, 119, **305** (1921); the phenomenon would appear to be closely related to the general inability, or very small tendency, of ketones to form six-membered cyclic ketals; Fischer and Pfähler, *Ber.*, 53,1606 (1920); Eoeseken, Schaefer and Hermans. *Rec. trav. chim.*, *41*, 722 (1922). That such can be formed is further evident from the recent work of Fischer and Taube, *Ber.*, *60*, 487 (1927), on the condensation of acetone with dioxyacetone.

[7] The structure of the three γ,δ-hydroxy ketones referred to in this communication is under investigation. Judging from analogy with the cyclic ketals, it seems probable that they will be found to be tautomeric mixtures of the free ketone with the butylene oxide ring isomer; in other words, the amylene oxide isomer is absent.

It is regretted that due to unavoidable delay the properties of the γ,δ-dihydroxy aldehydes have not as yet been investigated. In the light of recent investigations by Hibbert and co-workers on the isomeric forms of the aryl and alkyl glycerols and the close analogy found to exist between these derivatives and carbohydrates, glucosides and polysaccharides, it seems to be more than likely that the aldehydes corresponding to the ketones discussed in this communication will be found to consist of a mixture of the free aldehyde together with the corresponding butylene and amylene forms of the aldehydrol, the last named being present in by far the largest amount.

It is proposed to push this work intensively, and to give a resumé of the bearing of cyclic acetal and ketal formation on the constitution and properties of carbohydrates and polysaccharides in a forthcoming publication. H. H.

[8] Charon, *Ann. chim. phys.*, [7] *17*, 217 (1899).

Conversion into Crotyl Bromide.—The method used was that employed for **the** manufacture of **allyl bromide.**[9]

Seventy-five grams of crotyl alcohol (containing, by bromine titration, 90% of the alcohol) was dropped slowly into a flask containing 258 g. of 48% hydrobromic acid and 78 g. of concentrated sulfuric acid, and the mixture, after digestion and stirring for a period of one hour, then distilled. The crude bromide (b. p. 95–110°) was washed with potassium carbonate, dried with fused calcium chloride and fractionated. The product boiled at 101–105° and was practically free from butyl bromide; yield, 69%.

Preparation of Crotyl Ethyl **Aceto-acetate.**—Seven and six-tenths grams of sodium was dissolved in 100 cc. of absolute alcohol, 44 g. of ethyl aceto-acetate added and the mixture well shaken. Forty-seven grams of crotyl bromide was then dropped slowly into the cooled mixture. After digesting for twelve hours on the steam-bath, the sodium bromide was filtered off and the alcohol removed by distillation. The product was taken up with ether, washed, then dried with fused calcium chloride. Removal of the ether and fractionation under reduced pressure yielded a colorless liquid, b. p. 135–139° (46 mm.); yield, 66%.

Synthesis of **Δ^{5-6}-Heptene-2-one.**—The saponification of the crotyl aceto-acetate was carried out by the method used by **Wislicenus**[10] in saponifying various substituted ethyl aceto-acetates with alcoholic potash.

Method.—Thirty-eight grams (one mole) of crotyl ethyl aceto-acetate was heated for four hours with 313 g. (2.75 moles) of a 10% solution of potassium hydroxide in absolute alcohol. The precipitated potassium carbonate was separated by filtration and the alcohol removed by slow, careful fractionation, using a column of beads. The product left (50–60 cc.) was cooled by adding a small amount of ice, and the solution acidified by the addition of 10% hydrochloric acid. The precipitated potassium chloride was removed by suction filtration, the salt washed with ether and the combined solution and ether washings diluted with about half of its volume of ether. After washing with sodium carbonate, then with water, it was dried with calcium chloride. The ether was removed, and several refractionations using a column of beads, gave a product, b. p. 150–152°; yield, 54%.

Preparation of Methyl **γ,δ-Dihydroxyl Amyl** Ketone.—This was prepared by oxidizing the Δ^{5-6}-heptene-2-one with a 2% aqueous solution of barium permanganate. The procedure gave only a 54% yield indicating that other oxidation products were formed.

Method.—Ten grams of the Δ^{5-6}-heptene-2-one was mixed with 100 cc. of water, cooled to 0° and a cooled solution of 14.6 g. of barium permanganate in 730 cc. of water slowly added during the course of three hours, the mixture being stirred vigorously throughout the addition. The solution was then filtered and the water removed by distillation at 40° under 20 mm. pressure. The residual oil in the flask was dissolved in chloroform, the solution filtered and the chloroform removed by evaporation. The product left was a pale yellow liquid boiling at 139–143° (10 mm.); yield, 54%.

Anal. Calcd. for $C_7H_{14}O_3$: C, 57.54; H, 9.59. Found: C, 57.99, 58.05; H, 9.01, 9.30.

Conversion of Methyl **γ,δ-Dihydroxy Amyl** Ketone into its **Anhydro** Derivative.—On warming the ketone with a trace of concentrated sulfuric acid, the viscosity of the liquid increased rapidly, resulting within a few minutes in the formation of a thick, resinous product. Water was given off during the process. A quantitative estima-

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[9] Adams, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1920, Vol. I, p. 3.

[10] Wislicenus, *Ann.*, 190, 280 (1878).

tion showed that the polymerized product was formed by the loss of one molecule of water from each molecule of the dihydroxy ketone.

Method.—Into a specially constructed tube there was introduced about 0.5 g. of the ketone and about 0.002 g. of concentrated sulfuric acid and the contents heated in a glycerine bath at about 90° in a slow stream of dry air until constant weight was obtained. The water eliminated was absorbed by connecting with a weighed drying tube containing fused calcium chloride.

Subs. 0.4481; H_2O, 0.0536; loss in weight of ketone product 0.0672 or 14.99%. Calcd. for loss of 1 molecule of water; 12.33. Found: 11.96.

Analysis of Resulting Resin.—This was washed with water to remove sulfuric acid and then carefully dried.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.62; H, 9.37. Found C, 65.32, 65.26; H, 9.18, 9.14.

The resin is insoluble in dilute alkali and acid but readily soluble in concentrated acids (H_2SO_4; HCl). It dissolves readily in the common organic solvents.

Molecular Weight. Sample I. 0.2414; benzene, 43.65; AT, 0.050'. Mol. wt., 553. Sample II. (slightly less pure), 0.2833, 0.1588, 0.1131, 0.0794; benzene, 21 80; AT, 0.110°, 0.062°, 0.044°, 0.031°. Mol. wt., 591, 588, 590, 588.

The carefully washed and dried resin from methyl γ,δ-dihydroxy butyl ketone gave the following results.

Anal. Substance, 0.0974, 0.0994, 0.1530, phenol, 25.07, 28.11, 28.11; AT, 0.070°, 0.068°, 0.093°. Mol. wt., 422, 395, 445.

A determination, using camphor as solvent [Rast, Ber., 54, 1979 (1921); 55B, 1051 (1922)] gave the surprisingly high value of 3706.

Ratio of camphor to resin, approximately 15:1. Subs., 0.0208; camphor, 0.3351; AT, 0.67' (mean of 14 readings); k = 40. Mol. wt., 3706.

Preparation of Methyl γ,δ-Dihydroxy *Iso*Valeryl Ketone.—T s ketone was prepared by two different methods starting with methyl heptenone as the raw material.

1. Methyl heptenone was oxidized with a dilute aqueous solution of potassium permanganate, exactly according to the directions of Harries.''

2. Methyl heptenone was first converted into methyl heptenone oxide by the action of benzoyl hydroperoxide,[12] and then allowed to combine with the theoretical amount of water by allowing it to stand in contact with water at ordinary temperature for two hours. The oxide is a colorless liquid, b. p. 148–150°, and reacts with water with great readiness at ordinary temperature; in fad, unless it is kept in a very tightly stoppered bottle, it will only remain pure for a short time. On seeding with a little of the solid ketone it crystallized immediately into a thick, white mass. The crude product melted at 64° but, on crystallization from ligroin, at 67-68', in agreement with the value found by Harries.[11]

Action of Heat on Methyl γ,δ-Dihydroxy *Iso*-Valeryl Ketone.—The ketone is readily converted into the oxide under the influence of heat at 150° with the formation of only a very small amount of resin. The same change takes place in the presence of a trace of concentrated sulfuric acid, but with the difference that the speed of reaction is much increased and there is slightly more resinification.

Method.—Five grams of the ketone was heated in a distilling flask at 150° (inside temperature). A mixture of water and methyl heptenone oxide distilled over. Ether was added to the distillate, the product dried with anhydrous sodium sulfate, the ether

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[11] Harries, *Ber.*, 35, 118 (1902).

[12] Prileschaeff, J. Russ. *Phys.-Chem. Soc.*, *43*, 609 (1911).

removed and the residue fractionated. There was obtained 3 g. of methyl heptenone oxide, b. p. 145–155°; yield, 60%.

0.9651 g. of the ketone was heated under the same conditions and the residue weighed. The brown resinous product amounted to 0.0704 g., equivalent to 7.29%.

Additional experiments in which quantities of 1 to 2 g. of the ketone were heated with small amounts of concentrated sulfuric acid (0.02 to 0.08 g.) under the same conditions, gave results similar to those under the influence of heat alone. There is, therefore, no pronounced tendency for dehydration and polymerization to a resinous product as in the case of methyl γ,δ-dihydroxy amyl ketone.

Summary

1. Attention is drawn to the important role, in the case of dihydroxycarbonyl derivatives, played by the hydroxyl groups in the γ,δ-positions to the carbonyl group.
2. It is found that methyl γ,δ-dihydroxy amyl ketone behaves similarly to methyl γ,δ-dihydroxy butyl ketone in that it readily undergoes dehydration and polymerization in the presence of a trace of concentrated sulfuric acid. The change corresponds to a loss of one molecule of water from each molecule of the dihydroxy ketone.
3. Under the same conditions methyl γ,δ-dihydroxy isovaleryl ketone readily undergoes dehydration with formation of methyl heptenone oxide and shows little tendency towards polymerization. The introduction of the second methyl group in the 6-position thus facilitates to a pronounced degree the splitting off of water from the two adjacent hydroxyl groups.
4. The bearing of such changes on the formation of polysaccharides such as cellulose is indicated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

2,7-DIMETHYLSULFONEFLUORAN, 2'-HYDROXY-5'-METHYLBENZOYL-2-BENZENESULFONIC ACID AND SOME OF THEIR DERIVATIVES

BY W. R. ORNDORFF AND I. T. BEACH[1]

RECEIVED DECEMBER 19, 1927 PUBLISHED MAY 5, 1928

Fluoran was discovered by Baeyer[2] and its constitution established by Meyer.[3] 2,7-Dimethylfluoran was first made by Drewson.[4] Sulfonephthaleins have been prepared by Remsen and his students[5] and also

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[1] From a dissertation presented by I. T. Beach to the Faculty of the Graduate School, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Baeyer, *Ann.*, 212, 347 (1882).

[3] Meyer, *Ber.*, 24, 1412, 3586 (1891).

[4] Drewson, *Ann.*, 212, 340 (1882).

[5] Remsen and co-workers, *Am. Chem. J.*, 6, 180 (1884); 9, 372 (1887); 11, 73 (1889); 16, 513, 328 (1894); 17, 352, 656 (1895); 20, 257 (1898).

in this Laboratory.[6] The only sulfonefluoran hitherto described appears to be the 3,6-dimethylsulfonefluoran prepared by Orndorff and Purdy.[7]

Since the reactions of the anhydride and the chlorides of o-sulfobenzoic acid with *o*-cresol and with m-cresol have been investigated, it seemed of interest to study the analogous reactions with p-cresol. The present investigation was undertaken for this purpose.

Experimental Part

The p-cresol used in this investigation was purified by redistillation. The redistilled material contained less than 0.01% of m-cresol. The saccharin was presented by the Monsanto Chemical Works. The acid ammonium salt of o-sulfobenzoic acid was prepared by the hydrolysis of saccharin, as described by Blackshear.[8] The anhydride of o-sulfobenzoic acid was made by the interaction of the acid ammonium salt of o-sulfobenzoic acid with thionyl chloride.[9]

Condensation of o-Sulfobenzoic Anhydride with *p*-Cresol; 2,7-Dimethylsulfonefluoran.—Mixtures of one molecular equivalent of o-sulfobenzoic anhydride with slightly more than two molecular equivalents of p-cresol were heated in a thermostatically controlled electric oven. No reaction occurred in the absence of a condensing agent. In the presence of zinc chloride a slow reaction was obtained, although the yield of sulfonefluoran was small. A maximum yield of approximately 20% of the theoretical was obtained by heating the reaction mixture for fifteen hours at a temperature of 121 to 123°. It is probable that the reaction proceeds in two steps: first, the formation of an intermediate acid and, second, the reaction of this acid with a second molecule of the cresol to form the sulfonefluoran. Since this method of preparing the sulfonefluoran is very tedious and gives low yields, it was abandoned in favor of the synthesis from the di-*p*-cresyl ester of *o*-sulfobenzoic acid, as described below.

Di-*p*-cresyl-*o*-sulfobenzoate.—This ester was prepared by the Schotten-Baumann reaction, employing p-cresol and the chlorides of *o*-sulfobenzoic acid (prepared by the method of List and Stein).[10] To a mixture of 100 g. of p-cresol and 300 cc. of water in a liter flask, a strong solution of sodium hydroxide was added until the p-cresol was completely dissolved. The chlorides freshly prepared from 100 g. of the acid ammonium salt were added in small portions, while the temperature was kept between 30 and 35°. After the addition of the chlorides, which required about one-half hour, the mixture was allowed to stand for two hours with occasional shaking and was then boiled under a reflux condenser for two hours. During the entire series of operations the mixture was kept alkaline by the frequent addition of sodium hydroxide. The final mixture was allowed to cool and the crude ester was filtered off and recrystallized from methyl alcohol. The yield was 70%. This ester is a colorless, crystalline substance which melts at 95.5°. Professor Gill of the Department of Geology describes the crystals as

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[6] Orndorff and Sherwood, THIS JOURNAL, 45, 486 (1923); Orndorff and Vose, 46, 1896 (1924); Orndorff and Cornwell, 48, 981 (1926); Orndorff and Purdy, 48, 2212 (1926); S. P. Jackson, *Thesis*, "Orthocresolsulfonephthalein and Some of Its Derivatives." 1920.

[7] Orndorff and Purdy, THIS JOURNAL, 48, 2212 (1926).

[8] Blackshear, *Am. Chem. J.*, 14, 455 (1892).

[9] Orndorff and Cornwell, THIS JOURNAL, 48, 983 (1926).

[10] List and Stein, *Ber.*, 31, 1648 (1898).

follows. "The triclinic tabular crystals were measured but were not studied optically. The angles between the pinacoids were determined with fair accuracy as follows: 100 to 001, 89° 1'; 001 to 010, 117° 59'; 100 to 010, 73° 54'."

Anal. Calcd. for $C_{21}H_{18}O_5S$: S, 8.39; C, 65.93; H, 4.75. Found: S, 8.34, 8.42; C, 66.56, 66.41, 66.20; H, 5.10, 5.22, 4.97.

p-Cresyl-benzoate-o-sulfonechloride.—The formation of the di-cresyl ester of *o*-sulfobenzoic acid involves two consecutive reactions; first, the reaction of the acid chlorides with one molecule of the cresylate to form *p*-cresyl-benzoate-*o*-sulfonechloride and, second, the reaction of this product with a second molecule of cresylate to form the ester. At moderate temperatures the principal product is the acid chloride; considerable quantities of the ester are formed only on boiling. If the reaction mixture obtained by the addition of the acid chlorides to the cresylate (as described above) is filtered before boiling, a pasty mass consisting of impure *p*-cresyl-benzoate-*o*-sulfonechloride is obtained. This may be purified by recrystallization from glacial acetic acid. The purified material crystallized in lustrous, colorless plates which melted sharply at 138°.

Anal. Calcd. for $C_{14}H_{11}O_4SCl$: Cl, 11.41; S, 10.32. Found: Cl, 11.45, 11.35; S, 10.42, 10.40.

The Sodium Salt of the Carbinolsulfonic Acid of 2,7-Dimethylsulfonefluoran.—Equal quantities of di-p-cresyl-o-sulfobenzoate and zinc chloride, together with a few drops of hydrochloric acid, were heated to 170°, with stirring, for forty-five minutes. The reaction mixture was boiled with a fairly large amount of water and filtered. The hot filtrate was made alkaline with sodium carbonate and again filtered, and the combined filtrate and washings were concentrated to a specific gravity (hot) of 1.05 and cooled. The sodium salt of the carbinolsulfonic acid of 2,7-dimethylsulfonefluoran crystallized in fine needles and was purified by two crystallizations from absolute alcohol. This product is a colorless, crystalline material, very soluble in water but insoluble in benzene or ether. It has a very bitter taste. On exposure to air and light it soon turns yellow superficially. The sodium salt is turned yellow by a mere trace of acid. Professor Gill describes these crystals as follows. "The colorless crystals show bright interference colors and parallel extinction with less optical elasticity in the direction of elongation. They are biaxial and probably monoclinic in crystal system. They show two directions of cleavage, parallel to the ends of the flattened columnar crystals, and along these cleavage planes cloudiness slowly develops as the substance is exposed to the air."

Anal. Calcd, for $C_{21}H_{17}O_6SNa\cdot 1^1/_2C_2H_5OH$: Na, 4.86; C_2H_5OH, 14.59. Found: Na, 4.79, 4.80; C_2H_5OH, 13.84, 14.19.

2,7-Dimethylsulfonefluoran.—By the addition of concentrated hydrochloric acid to a hot, saturated solution of the sodium salt, pure 2,7-dimethylsulfonefluoran was precipitated as a mass of fine, orange needles. The crystals were washed with cold water and dried in the air.

2,7-Dimethylsulfonefluoran chars, without melting, at about 250". It is rather soluble in hot water but only slightly soluble in cold water. It dissolves readily in glacial acetic acid and in methyl or ethyl alcohol but does not crystallize well from these solvents. Large crystals were obtained by allowing a solution in hydrochloric acid to evaporate spontaneously. The solution in concentrated sulfuric acid has the green fluorescence characteristic of compounds containing the pyrone ring.

Professor Gill describes the crystals as follows. "The thick tabular red crystals are triclinic. In thin fragments the color is yellow with a distinct pleochroism, yellow to orange. The substance is optically biaxial with medium double refraction, the pleochroism is not observable in crystals thick enough to be blood-red in color."

Anal. Calcd. for $C_{21}H_{18}O_4S$: C, 69.19; H, 4.43; S, 8.80. Found: C, 69.08, 69.12; H, 4.52, 4.54; S, 8.81, 8.86.

Since the sulfonefluoran is colored, it is probably either an inner oxonium salt or an inner carbonium salt with o-quinoid or *p*-quinoid structure. There is no evidence to show which of these possible formulas is the correct one.

The PH value of 2,7-dimethylsulfonefluoran was determined by the use of standard buffer solutions. A sharp change from yellow to colorless took place between PH = 9.6 and PH = 10.0. When *a* strong solution of sodium hydroxide was added to an aqueous solution of the sulfonefluoran a deep blue color developed immediately. This color was very transient, fading in a few seconds. Because of the instability of the blue compound it could not be isolated.

Fusion of 2,7-Dimethylsulfonefluoran with Sodium Hydroxide.—In order to verify the structure assigned to the sulfonefluoran, the products obtained by fusion with sodium hydroxide were identified. Five grams of the salt of the carbinolsulfonic acid of the sulfonefluoran was mixed with 25 g. of sodium hydroxide and 10 g. of water and the mixture was heated for two hours at 200–220°. When the fused mass was poured into water the excess alkali dissolved, leaving a residue which was identified as 2,7-dimethyl xanthone. It had a melting point of 142° and dissolved in concentrated sulfuric acid to give a solution with a blue-green fluorescence. The formation of a xanthone under these conditions is evidence of the stability of the pyrone ring in the compound. When the fusion was made at a higher temperature (280–290°) the fusion mass was almost completely soluble in water. When the solution was acidified, sulfur dioxide was evolved and, on cooling, a crop of needle-like crystals was obtained. The crystalline material was identified as parahomosalicylic acid. It melted at 150° and gave an intense violet color with a solution of ferric chloride.

Action of Hydrogen Chloride, Ammonia and Bromine on **2,7-Dimethylsulfonefluoran.**—The 2,7-dimethylsulfonefluoran absorbed exactly one molecule of dry hydrogen chloride. On standing over sodium hydroxide, the hydrogen chloride was given off again. The sulfonefluoran did not absorb dry ammonia. The 2,7-dimethylsulfonefluoran gives a bromine addition product of variable composition. In this respect it differs from the isomeric compound prepared by Orndorff and Purdy, which readily forms a definite dibromo derivative.

Other Derivatives.—In addition to the above described derivatives, the following were also prepared: the barium salt of the carbinolsulfonic acid, colorless needles, containing four molecules of water of crystallization (by precipitation of the sodium salt with barium chloride); the methyl ester of the carbinolsulfonic acid, fine colorless crystals, very unstable (by heating the sulfonefluoran with dimethyl sulfate); the perchlorate, fine yellow crystals (by heating a solution of the sulfonefluoran in chlorobenzene with perchloric acid).

Reduction of **the Sulfonefluoran.**—To a liter of boiling water containing 2 g. of zinc dust, 5 g. of the sulfonefluoran was added in small portions. The orange color of the sulfonefluoran disappeared almost immediately after each addition. The excess zinc was filtered off and the filtrate cooled, whereupon a bulky, colorless precipitate formed. This was found to be the zinc salt of 2,7-dimethylhydrosulfofluoranic acid.

Anal. Calcd. for $(C_{21}H_{17}O_4S)_2Zn$: Zn, 8.22; S, 8.06. Found: Zn, 8.10, 8.18; S, 7.99, 8.04.

The free acid was liberated by the action of concentrated hydrochloric acid on the zinc salt, but it proved to be so unstable that no satisfactory analysis was obtained. It oxidized readily in the air to the sulfonefluoran.

2'-Hydroxy-5'-methylbenzoyl-2-benzenesulfonic Acid.—The ammonium salt of this the intermediate acid, was made by the method of Ullmann and Schmidt.[11] Twenty-seven g. of the anhydride of o-sulfobenzoic acid, 25 g. of p-cresol and 170 cc. of acetylene tetrachloride were heated in a round-bottomed flask, connected with a reflux condenser, on an oil-bath to 100–105°. Then 60 g. of aluminum chloride was added in small portions over a period of an hour and a half, and heating continued at 105–110° for one hour longer. The fused mass was poured into water and subjected to steam distillation. The solution remaining in the flask was freed from pitch by filtration and ammonium hydroxide added to alkaline reaction. The precipitated aluminum hydroxide was filtered off, washed with hot water and the combined filtrate and washings concentrated to crystallization. The product was freed from ammonium chloride by two recrystallizations from water. Professor Gill described these crystals as follows. "The larger stout columnar crystals and the finer (blade-like) needles show parallel extinction. This suggested rhombic crystallization but measurements of the angles on a reflecting goniometer by Dr. D. W. Trainer show that they are doubtless monoclinic elongated in the direction of the ortho axis probably of axial sphenoidal (sphenoidal, Groth) symmetry, since the ends seem to show good faces at only one extremity. The approximate angles in the zone of the ortho axis may be given as 30" 9', 60° 19', 38° 6' and 51° 26', and the angle between the end faces is 62° 34'. Double refraction is very strong and the biaxial character is certain."

Anal. Calcd. for $C_{14}H_{11}O_5SNH_4$: S, 10.37; N, 4.53. Found: S, 10.55, 10.46; N, 4.57, 4.58.

The free intermediate acid was obtained from the ammonium salt in the following manner. The ammonium salt was suspended in anhydrous ether and dry hydrogen chloride passed in, keeping the temperature below 10°. The ammonium chloride was filtered off and the ethereal solution quickly evaporated to dryness. A sirup resulted which solidified in a few hours. When this solid was dried on a porous plate, a crystalline powder was obtained. The intermediate acid has a melting point of 90°. It is unstable, decomposing to p-cresol and o-sulfobenzoic anhydride. Fused with potassium hydroxide it yields *p*-homosalicylic acid, the substance which was obtained from the sulfonefluoran under similar conditions. Heated with p-cresol the intermediate acid reacts to form 2,7-dimethylsulfonefluoran.

Anal. Calcd. for $C_{14}H_{12}O_5S$: Mol. wt., 292.16; S, 10.97. Found: Mol. wt., 291.6, 294.7, 298.9; S, 10.89, 11.01.

2,7-Dimethylsulfonecoeroxonol.—Ten g. of the sulfonefluoran was dissolved in 200 g. of concentrated sulfuric acid and the solution was heated at 200° for two hours. The cooled solution, which was deep red, was poured into 200 g. of ice. A small amount of insoluble matter was then filtered off and the solution was added to a mixture of am-

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[11] Ullmann and Schmidt, Ber., 52, 2098 (1918).

monium hydroxide and ice. A bulky, brownish precipitate resulted which was filtered off, washed and dried. This substance resembles the coeroxonols made by Ferrario.[12] It is insoluble in water and ether, somewhat soluble in benzene, xylene and alcohol and very soluble in acids, with an intense red color. Hence it was called 2,7-dimethylsulfonecoeroxonol.

Anal. Calcd. for $C_{21}H_{16}O_4S$: S, 8.80. Found: S, 8.65, 8.63.

Summary

The results of this investigation may be summarized as follows.

1. 2,7-Dimethylsulfonefluoran has been prepared both by the condensation of o-sulfobenzoic anhydride with *p*-cresol and by the fusion of di-*p*-cresyl-*o*-sulfobenzoate with zinc chloride. The latter method gave the better yield.

2. 2,7-Dimethylsulfonefluoran is a colored substance and hence is supposed to have a quinoid structure. It may be represented either as an inner oxonium or inner carbonium salt.

3. On fusion with sodium hydroxide, 2,7-dimethylxanthone and *p*-homosalicylic acid are produced. The formation of these substances is in accord with the structure assigned to the sulfonefluoran.

4. Unlike fluorans and the only other sulfonefluoran mentioned in the literature, 2,7-dimethylsulfonefluoran forms salts and esters. The sodium and barium salts and the methyl ester have been prepared. These are derived from the carbinolsulfonic acid form of the fluoran and are colorless.

5. Two derivatives of the colored form have been prepared, the hydrochloride and the perchlorate.

6. 2,7-Dimethylsulfonefluoran behaves as an indicator. The change from yellow to colorless takes place at a PH of 9.6–10.0.

7. 2,7-Dimethylhydrosulfofluoranic acid has been made by the reduction of the sulfonefluoran. This compound is colorless.

8. The intermediate acid, 2'-hydroxy-5'-methylbenzoyl-2-benzenesulfonic acid has been made by the Ullmann and Schmidt method, which consists in condensing o-sulfobenzoic anhydride with *p*-cresol in acetylene tetrachloride in the presence of aluminum chloride. The acid is unstable, decomposing to give *p*-cresol and the anhydride of o-sulfobenzoic acid.

9. Heating the sulfonefluoran with sulfuric acid causes the elimination of a molecule of water with the formation of 2,7-dimethylcoeroxonol.

ITHACA, NEW YORK

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[12] Ferrario, *Ann.*, 348, 213 (1906).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

THE INTERACTION OF HYDROGEN SULFIDE WITH CERTAIN AMINO AND IMINO ACID NITRILES

BY ELIZABETH GATEWOOD[1] AND TREAT B. JOHNSON

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The organic chemist who directs his attention to the study of biochemical changes functioning in the early stages of natural cellular syntheses meets at the start with some very puzzling phenomena of fundamental importance. He is confounded by the problems presented for solution due to the limitations of our present knowledge of the conditions normally effecting and regulating the activity of the simple compounds like carbon dioxide, ammonia, hydrocyanic acid and hydrogen sulfide; and is called upon to interpret puzzling chemical phenomena involving these compounds which are extremely susceptible to mild physical and chemical treatment.

As the science of biochemistry is developed we are continually being introduced to new chemical mechanisms which are apparently regulated or controlled by chemical and physical influences entirely different from those met with in laboratory technique, and in the newer interpretations and postulations made to advance our knowledge we are compelled to conceive of chemical interchanges that would not at first be considered of any biochemical significance. When we stop to consider, however, the chemical significance of some of the remarkable chemical transformations easily accomplished by living cellular organisms we are then forced to admit that the mechanisms involved in such metabolic processes are well worthy of very thoughtful study.

In our preliminary study of the fundamental chemical changes taking place in bacillary growth we have continually been brought into close touch with obscure phenomena characterizing biochemical change, and the observations we have already made in the field of tuberculosis have forcibly suggested to us that simple water soluble substances like ammonia, carbon dioxide and hydrocyanic acid may be of as much fundamental importance in the life of the growing bacterial cell as the more complex colloidal bodies upon which greater emphasis is usually placed by present day investigators.

In consequence of the growing interest in the biochemistry of sulfur in organic combination, it is very desirable that we have an understanding of the chemical behavior of hydrogen sulfide toward nitriles of amino and imino acids. It is believed that amino nitriles, for example, play a far more important role in natural synthetic processes than commonly assumed, and very probably function in the early stages of protein synthesis

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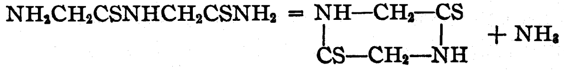
[1] Holder of the Metz Research Fellowship in Chemistry, 1926–27.

from simpler substances. It is well known that the —CN group of certain combinations is very susceptible to chemical change when exposed to the action of hydrogen sulfide, and it seems not improbable that hydrogen sulfide may be the first assimilation product of inorganic sulfates, and that certain amino thioamides actually function in the natural synthesis of sulfur proteins. The conception of the thiopolypeptide structure was expressed in a publication by the senior author as early as 1910,[2] and since that time many facts have been revealed which have confirmed the idea that the —CS·NH— grouping is one of the fundamental constructions functioning in nature.

In 1911 Johnson and Burnham[3] contributed the first paper on this subject and reported results obtained when hydrogen sulfide is allowed to interact with the simplest nitrile of an amino acid, namely, amino-acetonitrile. While these reagents do not interact smoothly, they found that the main product of combination was 2,5-dithiopiperazine. Gatewood and Johnson[4] repeated this work, and in a later publication confirmed the conclusion of the original investigators. Johnson and Burnham considered the dithiopiperazine as the final product of a series of changes and interpreted the course of the reaction according to the following scheme. The nitrile of α-alanine (aminopropionitrile) is known to interact

$$\mathrm{NH_2CH_2CN + H_2S = NH_2CH_2CSNH_2}$$

$$\mathrm{2\ NH_2CH_2CSNH_2 = NH_2CH_2CSNHCH_2CSNH_2 + NH_3}$$



$$\mathrm{NH_2CH_2CSNHCH_2CSNH_2} = \begin{array}{l} \mathrm{NH{-}CH_2{-}CS} \\ \,|\qquad\quad\ \ | \\ \mathrm{CS{-}CH_2{-}NH} \end{array} + \mathrm{NH_3}$$

in a similar manner with hydrogen sulfide to form 3,6-dimethyl-2,5-dithiopiperazine whose physiological action has previously been reported in a publication by Lewis.[5] Of all the nitriles we have thus far examined in this Laboratory, these are the only two that have been observed to interact with hydrogen sulfide to form dithiopiperazines.

The yield of dithiopiperazine from aminopropionitrile is exceedingly small as this change does not represent the primary reaction in this case, as will be shown below. The experimental evidence thus far accumulated, therefore, does not permit us to draw the conclusion that the formation of dithiopiperazines is a general reaction when nitriles of amino acids are allowed to interact with hydrogen sulfide. Two other characteristic reactions of equal significance have been revealed as a result of our researches in this field.

The action of hydrogen sulfide on four nitriles of amino acids and three imino nitriles has now been studied and their behavior toward this reagent

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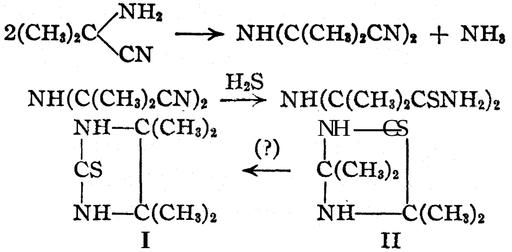
[2] Johnson and Burnham, J. *Biol. Chem.*, 9,331 (1911).

[3] Johnson and Burnham, *ibid.*, 9, 449 (1911).

[4] Gatewood and Johnson, THIS JOURNAL, 48,2900 (1926).

[5] H. B. Lewis, J. *Bid. Chem.*, 14, 255 (1913).

are recorded in this paper. The most outstanding result of this research has been the discovery of the unique behavior of hydrogen sulfide toward amino-isobutyronitrile. These reagents interact to give a definite and well defined crystalline substance whose structure we have not established with absolute certainty. The compound is not a dithiopiperazine, neither is it amino-isobutyrothio-amide nor the corresponding thiopolypeptide. It has the empirical formula $C_7H_{14}N_2S$, indicating that two molecules of the nitrile interact with hydrogen sulfide with loss of one carbon and two nitrogen atoms. Provisionally the structure of 2,2,4,4-tetramethyl-5-thio-2-desoxyhydantoin (II) has been assigned to it. So far as we are aware no sulfur cyclic combination of this type has hitherto been described in the literature. The course of the reaction may be formulated in the following manner



$$2(CH_3)_2C\begin{matrix}\nearrow NH_2\\ \searrow CN\end{matrix} \longrightarrow NH(C(CH_3)_2CN)_2 + NH_3$$

$$NH(C(CH_3)_2CN)_2 \xrightarrow{H_2S} NH(C(CH_3)_2CSNH_2)_2$$

I II

That the first step of this change involves the formation of an imino nitrile with loss of ammonia as represented above, is confirmed by the fact that pure iminodi-*iso*butyronitrile interacts with hydrogen sulfide to give the same end product. The possibility of a molecular rearrangement can also be postulated here and the compound be assigned the constitution of a reduced thioglyoxaline as represented by Formula I. This structure is, however, excluded as the compound is soluble in both alkali and acids and undergoes hydrolysis smoothly when heated with hydrochloric acid, giving amino-isobutyric acid.

All three compounds, amino-acetonitrile, a-aminopropionitrile, and a-amino-isobutyronitrile lose ammonia on heating, their stability increasing, however, with increase in molecular weight. Amino-acetonitrile cannot be distilled without decomposition; aminopropionitrile can be distilled under diminished pressure but on standing it soon loses ammonia, giving the iminonitrile. Amino-isobutyronitrile is more stable and decomposes only slightly when distilled at ordinary pressure. The corresponding imino compound is formed only after standing for several days. In other words, these three compounds are sharply differentiated by their degree of stability. In correlation to this difference in degree of stability is the characteristic behavior of each type toward hydrogen sulfide. Amino-acetonitrile interacts with this reagent to form a dithiopiperazine, aminopropionitrile interacts to form predominantly iminodipropionitrile, while the amino-*iso*butyronitrile gives a reduced isodiazole combination. As the molecular weight of the nitrile is increased further, not only do we meet with greater stability but also with less reactivity toward hydrogen sulfide. For example, α-aminomethylethylacetonitrile and α-aminodiethylacetonitrile are both very stable, giving no ammonia on distillation, and furthermore failing to react with hydrogen sulfide even when heated under pressure. Possibly steric hindrance in the molecule may be a factor here, influencing the reactivity of these two compounds.

The three imino nitriles examined do not agree in their chemical behavior toward hydrogen sulfide. Iminodiacetonitrile interacts to form three different products. One melts at 124° and is probably the corresponding thio-amide giving, by analysis, the required percentage of nitrogen. The second product formed in this reaction melts at 186° and yields analytical results for nitrogen agreeing with that calculated for 5-thio-2-desoxyhydantoin. The carbon and hydrogen determination, however, gave results altogether too low for this compound. A third product seems to be formed also but it had no definite melting point, was amorphous and could not be obtained in a condition sufficiently pure for an analysis. Iminodipropionitrile was never observed to interact with hydrogen sulfide and in every experiment tried was recovered unaltered. On the other hand, as stated above, the iminodi-isobutyronitrile interacts with hydrogen sulfide to give the same product as amino-isobutyronitrile, namely, 2,2,4-4-tetramethyl-5-thio-2-desoxyhydantoin (II).

It is a very interesting fact that amino-acetonitrile and iminodiacetonitrile do not react with hydrogen sulfide to form the same sulfur combination, as was observed in the case of amino-isobutyronitrile and its corresponding imino derivative.

Experimental Part

The Action of Hydrogen Sulfide on α-Amino-*iso*butyronitrile, 2,2,4,4-Tetramethyl-5-thio-2-desoxyhydantoin.—A solution of 20 g. of the hydrochloride of this nitrile[6] in 100 cc. of absolute alcohol and 50 cc. of concentrated aqueous ammonia, or 20 g. of the pure nitrile in 75 cc. of absolute alcohol and 25 cc. of concentrated aqueous ammonia, was cooled with ice and salt and saturated with hydrogen sulfide. Under the first condition ammonium chloride separates and is removed by filtration when the reaction is complete. The almost colorless solution is allowed to evaporate spontaneously, when a crystalline product is obtained. This was purified by crystallization from boiling water and melted at 153–155°. The yields obtained were 5.4 and 7.0 g., respectively, and were not increased by using gaseous ammonia in large excess.

Anal. Calcd. for $C_7H_{14}N_2S$: C, 53.1; H, 8.9; N, 17.7 Found: C, 52.7, 53.0; H, 8.6, 8.7; N, 17.8, 17.6.

The reaction product contains sulfur. It is difficultly soluble in cold water and soluble in hot water, alcohol and ether. The hydantoin dissolves readily in both acid

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[6] Gulewitsch and Wasmus, *Ber.*, 39, 1181 (1906); Dubsky, *Ber.*, 49, 1136 (1916).

and alkali solutions and is slowly decomposed with generation of hydrogen sulfide when boiled vigorously with these reagents. The sulfur is extremely firmly bound in this combination. Phosphotungstic acid and sodium nitroprusside tests for sulfur were negative. Also the compound can be refluxed in alcohol with mercuric oxide without loss of sulfur. It forms a mercury salt which crystallizes from ether and melts at 175'. By interaction of this salt with hydrogen sulfide the original hydantoin melting at 155° is regenerated. The hydantoin interacts with chloro-acetic acid giving an oily compound which could not be distilled.

The hydantoin undergoes hydrolysis when digested with concentrated hydrochloric acid, giving the hydrochloride of a-amino-isobutyric acid,[7] melting at 230'. The free amino acid was isolated by treatment of this hydrochloride with silver oxide and hydrogen sulfide successively, and exhibited all the properties of the known acid, possessing a sweet taste and subliming at 280° without decomposition.

Action of Hydrogen Sulfide on α-Aminopropionitrile (Iminodipropionitrile).—A solution of 5 g. of the above nitrile[8] dissolved in 50 cc. of concentrated alcoholic ammonia was saturated at 0° with hydrogen sulfide and allowed to stand for several hours. The solution was then allowed to evaporate spontaneously in a vacuum desiccator, when a crystalline substance finally separated admixed with some oil which was undistillable. This solid was identified as iminodipropionitrile and after crystallization from ether melted at 67–68°.[8] Several experiments were performed under variable conditions using ammonia in aqueous and alcohol solutions of different concentrations and at various temperatures but in every case the chief product of reaction was the iminonitrile. It is possible that the yellow oil which always accompanies this product was a thio-amide combination but it was so unstable that no method of purification could be devised.

a-Aminomethylethylacetonitrile and a-aminodiethylacetonitrile were prepared according to the directions of Biltz and Slotta[9] with only one change in technique, namely, substitution of ammonium chloride for ammonium sulfate in preparing the nitrile from the corresponding ketones—methyl ethyl and diethyl ketones. Both of these nitriles are very stable and can be kept indefinitely without change. Both compounds revealed themselves as inactive nitriles when exposed to the action of hydrogen sulfide in alcohol–ammonium solution. In all our experiments unaltered nitrile was recovered even when we operated at a temperature as high as 60–70°.

Action of Hydrogen Sulfide on Iminodiisobutyronitrile, 2,2,4,4-Tetramethyl-5-thio-2-desoxyhydantoin (II).—A solution of 8.5 g. of this iminonitrile[3] was dissolved in a mixture of 50 cc. of absolute alcohol and 20 cc. of concentrated ammonia and the solution then saturated with hydrogen sulfide at 0°. After allowing it to stand for several hours and then evaporating, we obtained 4.6 g. of the crystalline desoxyhydantoin melting at 153–155'. A mixed melting point and its properties showed that this was identical with the substance obtained by the action of hydrogen sulfide on the α-amino-*iso*butyronitrile.

Several attempts were made to bring about an addition of hydrogen sulfide to iminodipropionitrile, but in no case were we able to obtain evidence of the formation of a thio-amide. The nitrile was recovered unaltered in every experiment tried.

Action of Hydrogen Sulfide on Iminodiacetonitrile.—A solution of 5 g. of this nitrile dissolved in a mixture of 250 cc. of concentrated aqueous ammonia was saturated with hydrogen sulfide and then allowed to stand in a closed flask for several hours. A bright yellow solution resulted. When this was allowed to evaporate at ordinary temperature, about 2.5 g. of a yellow, crystalline substance finally separated. On ex-

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[7] Zelinsky and Stadnikoff, Ber., 39, 1726 (1906).

[8] Dubsky, Ber., 49, 1048 (1916).

[9] Biltz and Slotta, *J. prakt. Chem.*, 113, 249 (1926).

amination this was found to be a mixture of two substances which we were able to separate mechanically The major portion was a deep yellow product, well crystallized and melting at 124°. The second substance began to blacken at 150° in the capillary tube and then melted at 186°. This compound proved to be easily soluble in water and could be freed from the compound melting at 124° by washing with this solvent. Of the purified compound melting at 124° we obtained 2.0 g. and of the higher melting compound 0.3 g. This experiment was repeated several times but without increasing the yield of the compound melting at 186°. The compound melting at 124° is easily purified by crystallization from methyl alcohol, while the 186° product is purified best by dissolving in cold water and then precipitating by dilution with alcohol. Both compounds evolved ammonia when dissolved in cold alkali, and hydrogen sulfide is liberated on acidifying the alkaline solution.

Anal. (Compound melting at 186°, 5-thio-2-desoxyhydantoin.) Calcd. for $C_3H_6N_2S$: N, 27.46. Found: N, 27.48, 27.45. (Compound melting at 124°, iminodiacetothioamide.) Calcd. for $C_4H_9N_3S_2$: N, 25.74. Found: N, 25.51, 25.54.

Summary

1. In our study of the chemical behavior of hydrogen sulfide toward nitriles of amino acids, we have thus far succeeded in revealing the following three characteristic types of reaction. (a) Formation of a dithiopiperazine as is illustrated in the action of hydrogen sulfide on aminoacetonitrile. (b) Molecular condensation with formation of an imino nitrile as is illustrated in the action of hydrogen sulfide on α-aminopropionitrile, giving the corresponding imino compound with loss of ammonia. (c) Formation of a thiodesoxyhydantoin as is illustrated in the action of hydrogen sulfide on amino-*iso*butyronitrile.

2. From the present evidence it is impossible to predict the course of the reaction which will take place when a given nitrile in this series of compounds is exposed to the action of hydrogen sulfide.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE PREPARATION AND PHYSICAL PROPERTIES OF α-, β- AND γ-BUTYLENE AND NORMAL AND ISOBUTANE

BY C. C. COFFIN AND O. MAASS

RECEIVED JANUARY 3, 1928 PUBLISHED MAY 5, 1928

Introduction

A number of the physical properties of hydrocarbons containing two and three carbon atoms have been accurately determined in this Laboratory.[1] The present paper describes an extension of this work to compounds of 4 carbon atoms, namely, the three butylenes and the two butanes. The preparation of these compounds is described and their boiling points, melting points and critical temperatures are tabulated. The vapor pressures, densities and surface tensions were determined over a wide

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[1] Maass and Wright, THIS JOURNAL, 43, 1093 (1921).

range of temperature. Great stress was laid upon the purity of the compounds and the accuracy of the measurements, since small differences in physical properties were to be expected in the case of the isomeric substances. No measurements were made in cases where reliable data were found to exist in the literature. The data obtained are discussed from the point of view of the effect of molecular attraction and constitution upon physical properties.

Preparation and Purification of the Hydrocarbons

α-Butylene was prepared by the action of an excess of alcoholic potash on n-butyl iodide, the evolved gas being collected over water in a gasometer. As it was found that the butylenes polymerized rapidly in the presence of phosphorus pentoxide, this substance could not be used as a drying agent. The following is a description of the method employed for the drying and purification of these compounds.

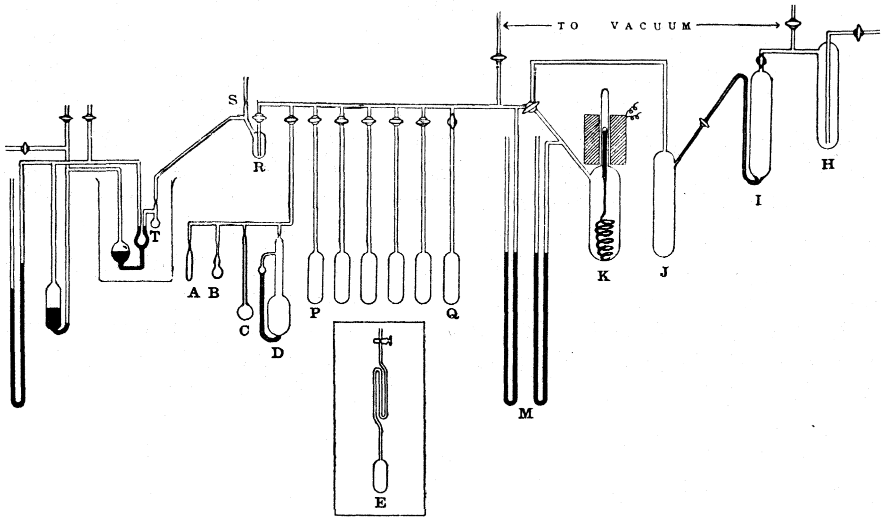

Fig. 1.

The butylene was condensed in H (Fig. 1) by means of carbon dioxide and ether and the system was evacuated. It was then distilled into I and the tap above it was closed. By opening the tap on the capillary between I and J and warming the upper part of I with the hand, the liquid was forced over into J, which was also surrounded with carbon dioxide and ether. In this way the liquid butylene was separated at −78" from the water which remained frozen to the sides of I. This was found to be more effective than fractionation in removing water. From J it was distilled to K for fractionation. The receivers (bulbs P to Q) were kept at −78°. The liquid in K was kept at −55 to 60° by means of an ether-bath cooled with carbon dioxide and stirred with a current of **dry** air. The liquid being fractionated was kept vigorously agitated by a magnetic stirrer. Under these conditions distillation proceeded slowly and a very satisfactory fractionation was obtained. By means of the manometers, M, the vapor pressures of any fraction or of the residue in K could be determined. Fractions of like vapor pressures were combined in K and refractionated. The heads and tails of each fractionation were rejected. The form of the receivers as shown at E was found to be very convenient. Their flexibility made it possible to agitate the contents when determining the vapor pressure of the fractions and enabled as many as three bulbs to be kept in the one Dewar flask for storage. The final constant boiling middle fraction was distilled into the critical temperature bulb, the melting point bulb, the dilatometer and the surface tension tube (A, B, C and D), which were then sealed off.

For identification purposes and as a test of the purity of the butylenes, the dibromide of the final middle fraction was made and its boiling point determined. A few drops of bromine were introduced into R through the tube S. R was cooled in ice and the butylene passed through until the bromine was decolorized. The tap on R was then closed. S was sealed off and the system was evacuated. A sufficient quantity of the dibromide was distilled into T, which was sealed off at the constriction just above the bulb. The vapor pressure curve of the dibromide was then determined in a manner described elsewhere.[2]

The product of the potassium hydroxide-n-butyl iodide reaction consisted of practically pure a-butylene boiling over a range of 0.2" at −6°. Several fractionations failed to isolate a higher or a lower boiling fraction. The final middle fraction taken as the pure compound boiled at −6.1°. The boiling point of the dibromobutane prepared from this fraction was 166°. (*I. C. T.* gives 166° as the boiling point of 1,2-dibromobutane).

β-Butylene was prepared by the method described by King.[3] The vapor of *n*-butyl alcohol was passed over lump pumice impregnated with glacial phosphoric acid. Dehydration proceeded rapidly at 250–280°. The product as indicated by the fractionation of a considerable quantity of the dibromide and of the condensed olefin itself was 85 to 90% β-butylene, the remainder being α-butylene. Some experiments on the dehydration of n-butyl alcohol by alumina at 250° gave a mixture of α- and β-butylene, the a-isomer predominating. It is worth mentioning that this is in agreement with the conclusion reached from some recent work on the dibromobutanes prepared in the same way.[4] The final middle fraction of the product from the phosphoric acid dehydration boiled at 1.0° and gave a dibromobutane boiling at 158°. These values are in good agreement with those in the literature for β-butylene and 2,3-dibromobutane.

γ-Butylene was prepared by the dehydration of isobutyl alcohol by alumina at 250 to 300° as described elsewhere.[5]

n–Butane was prepared by the hydrogenation of α- and β-butylene over a nickel catalyst. Small-mesh pumice was impregnated with nickel hydroxide precipitated from nickel nitrate (+1% of silver nitrate) solution with sodium hydroxide. The pumice with the adhering hydroxide was washed free of soluble salts, dried at 100" and reduced in the catalyst tube with hydrogen at 300°. The butylenes were hydrogenated at 150–200° and the butane was purified by slowly passing it a number of times through bromine, potassium hydroxide, sulfuric acid and phosphorus pentoxide. The product was then condensed and fractionated as described above.

***Iso*butane** was prepared in the same way by the hydrogenation of γ-butylene. These butane preparations afford a check on the purity of the butylenes. a-Butylene prepared from the iodide gave pure n-butane. A compound with identical properties was obtained when the products of the dehydration of n-butyl alcohol by alumina and phosphoric acid (a mixture of α- and β-butylenes) were hydrogenated in the same way.

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[2] Sutherland and Maass, Trans. Roy. *Soc.* (Canada), 20,499 (1926).

[3] King, *J. Chem.* Soc., 115, 1401 (1920).

[4] Lépingle, *Bull. soc. chim.*, 39, 741 (1926).

[5] Coffin and Maass, Trans. Roy. *Soc.* (Canada), 21, 33 (1927).

No γ-butylene is therefore formed in these preparations from *n*-butyl alcohol. That pure isobutylene is formed by the dehydration of *iso*butyl alcohol with alumina was proved by the fact that this olefin was hydrogenated to pure isobutane.

Determination of Physical Properties

Temperatures below —30° were measured with a platinum resistance thermometer calibrated at the ice, carbon dioxide and oxygen points.

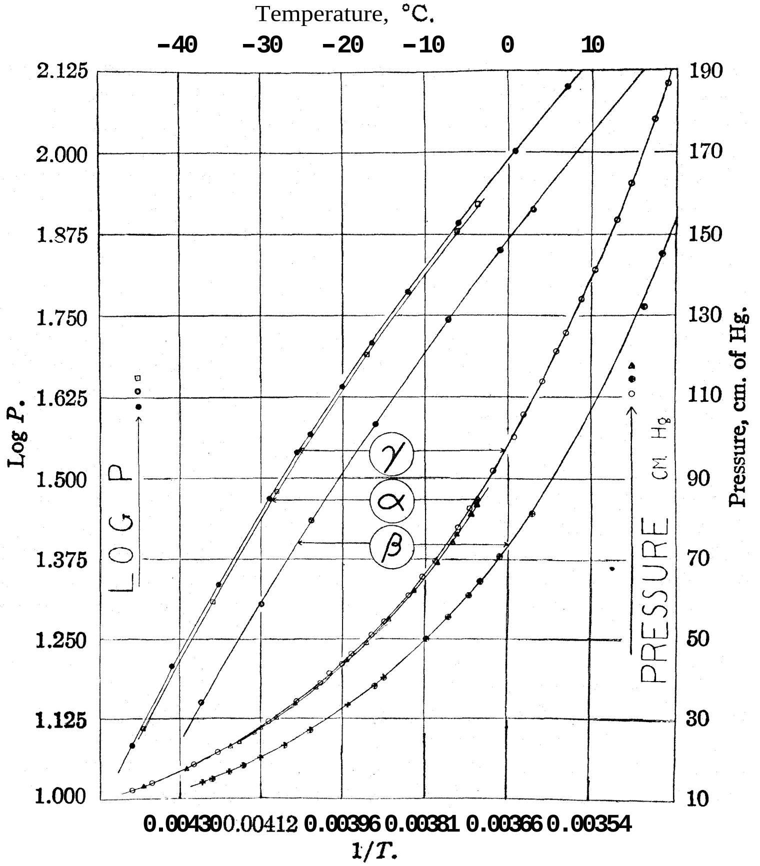
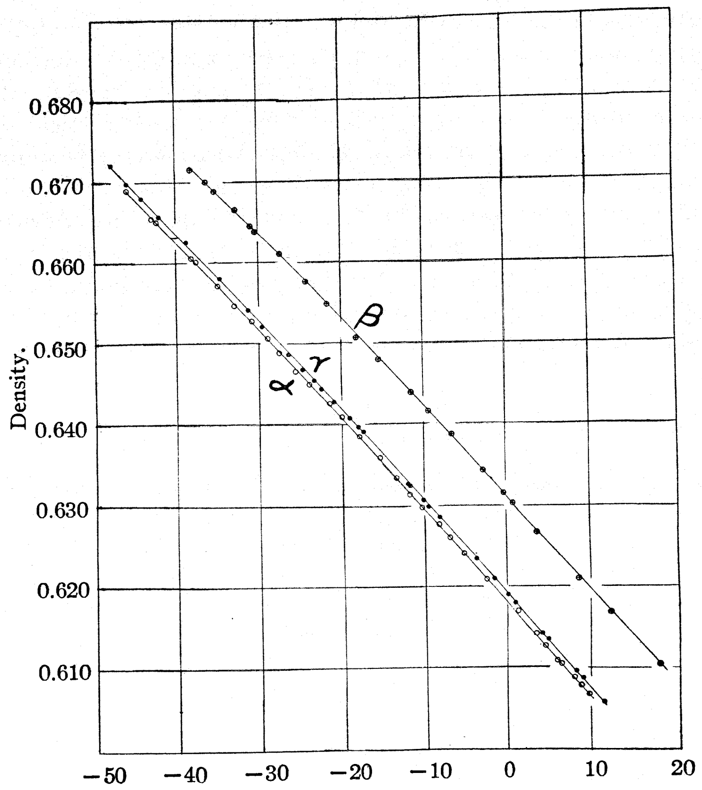


Fig. 2.

Intermediate temperatures were calculated by means of the Callendar–Barnes formula. The calibrations were checked from time to time. This thermometer agreed to within 0.1° with a standard mercury thermometer over the range 0 to 36°, so that all temperature measurements are probably correct to within at least 0.2'. Temperatures above —30° were measured with standard mercury thermometers graduated in tenths.

The constant temperature baths and the methods of determining density, surface tension, vapor pressures, melting points and critical



a = α-Butylene; β = β-butylene; γ = γ-butylene.

Fig. 3.

TABLE I

VAPOR PRESSURES OF α- AND β-BUTYLENE

α-Butylene				β-Butylene			
Temp., °C.	Press., cm. Hg	Temp.. °C.	Press., cm. Hg	Temp.. °C.	Press., cm. Hg	Temp., °C.	Press., cm. Hg
−3.7	83.37	−28.0	30.29	20.4	155	−23.8	27.22
−4.4	81.14	−29.9	27.69	18.3	145	−27.0	23.33
−6.1	76.02	−32.6	24.22	16.2	132	−30.0	20.14
−6.7	74.02	−33.7	23.00	2.9	81.4	−32.1	18.15
−8.5	69.13	−39.2	17.53	−1.0	70.74	−33.9	16.57
−11.3	62.17	−44.6	13.08	−3.3	64.46	−36.0	14.92
−14.3	54.96	−52.3	8.33	−4.7	60.98	−37.2	14.07
−17.0	49.13	−57.1	6.20	−7.1	55.52	−40.2	11.88
−19.4	44.51	−60.1	5.05	−9.7	49.97	−47.1	7.96
−23.1	37.77	−77.5	2.35	−14.9	40.27	−53.8	5.33
−25.6	33.80			−16.0	38.32	−60.1	3.53
				−19.2	33.47	−66.8	2.19
				−22.3	32.50		

temperatures were in the main those described by Maass and Wright.[1] The surface tension tube, of the type recommended by Richards, was carefully calibrated with dry ether and a mercury thread. Readings were made through a telescope and the tube was kept vertical by means of plumb bobs. As a great many readings were taken, the temperature range being covered at least twice for each substance, the values given in the table are those picked from the smooth temperature surface tension curve at 5° intervals. The weight of the substance in the vapor state and the expansion of the glass of the dilatometer were taken into account in the density determinations, for which an accuracy of one part in 2000 is claimed. All fractionations and measurements were made in the ab-

TABLE II

DENSITIES OF α- AND β-BUTYLENE AND NORMAL AND *ISO*BUTANE

α-Butylene		β-Butylene		*n*-Butane		*Iso*butane	
Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density
9.8	0.6067	17.8	0.6105	32.5	0.5644	25.3	0.5530
8.9	.6077	14.3	.6146	29.3	.5681	20.2	.5591
8.1	.6088	12.3	.6169	26.5	.5715	12.5	.5682
6.6	.6105	8.6	.6210	23.3	.5753	11.7	.5691
6.1	.6109	5.9	.6216	18.8	.5805	8.5	.5729
4.7	.6127	3.8	.6267	15.5	.5844	4.3	.5787
3.6	.6142	1.7	.6289	13.7	.5865	0.7	.5821
1.9	.6158	0.9	.6303	8.5	.5928	−1.3	.5845
−0.5	.6170	−0.3	.6315	1.3	.5998	−2.7	.5857
−1.4	.6189	−2.8	.6345	−0.8	.6020	−5.5	.5893
−2.5	.6209	−4.2	.6355	−3.5	.6048	−6.2	.5899
−4.1	.6229	−6.6	.6387	−6.7	.6081	−8.5	.5924
−5.2	.6241	−9.4	.6416	−10.5	.6121	−11.2	.5957
−6.9	.6261	−11.5	.6439	−14.4	.6159	−13.6	.5980
−8.2	.6277	−13.0	.6454	−19.0	.6207	−15.8	.6005
−10.3	.6298	−15.5	.6480	−24.6	.6265	−20.7	.6055
−11.8	.6314	−18.2	.6507	−30.2	.6318	−27.8	.6131
−13.4	.6334	−21.8	.6549	−32.8	.6346		
−15.4	.6359	−24.4	.6576	−34.4	.6362		
−17.9	.6385	−27.5	.6611				
−20.0	.6409	−30.4	.6638				
−21.5	.6426	−32.8	.6666				
−24.0	.6450	−35.3	.6689				
−25.7	.6466	−36.3	.6700				
−27.6	.6489	−38.2	.6715				
−29.0	.6507	−42.4	.6746				
−30.9	.6528						
−33.0	.6547						
−35.0	.6571						
−38.2	.6606						
−42.4	.6651						
−43.0	.6655						
−46.0	.6690						

sence of air and moisture and glass sealed connections were used throughout. All temperatures and pressures are corrected to standard conditions.

Vapor pressures are given in Table I, densities in Table II and surface tensions in Table III. The comparison of the isomers is best brought out by the graphs, Figs. 2 to 6, to which the values of y-butylene previously published have been added. Figs. 4 and 6 show the variation of molecular surface energy with the temperature.

TABLE III

SURFACE TENSIONS OF α- AND β-BUTYLENE AND NORMAL AND *Iso*BUTANE

α-Butylene		β-Butylene	*n*-Butane		*Iso*butane	
Temp., °C.	γ, dynes	γ, dynes	Temp., °C.	γ, dynes	Temp., °C.	7, dynes
20	12.60	13.51	29.7	11.28	23.3	9.80
15	13.21	14.16	26.0	11.67	19.1	10.51
10	13.85	14.82	18.7	12.58	12.4	11.39
5	14.49	15.49	10.1	13.64	9.8	11.61
0	15.14	16.15	0.5	14.88	4.5	12.31
−5	15.81	16.74	−2.4	15.21	−1.0	12.30
−10	16.46	17.42	−4.5	15.43	−8.5	13.81
−15	17.14	18.01	−7.8	15.77	−11.0	14.01
−20	17.82	18.70	−10.4	16.01	−15.0	14.80
−25	18.50	19.30	−15.0	16.72	−19.0	15.07
−30	19.20	20.00	−17.8	16.95	−24.4	15.96
−35	19.80	20.61	−28.1	18.21	−30.0	16.55
−40	20.50	21.22	−36.1	19.22	−36.3	17.30
−45	21.13	21.84				
−50	21.85	22.57				
−55	22.48					

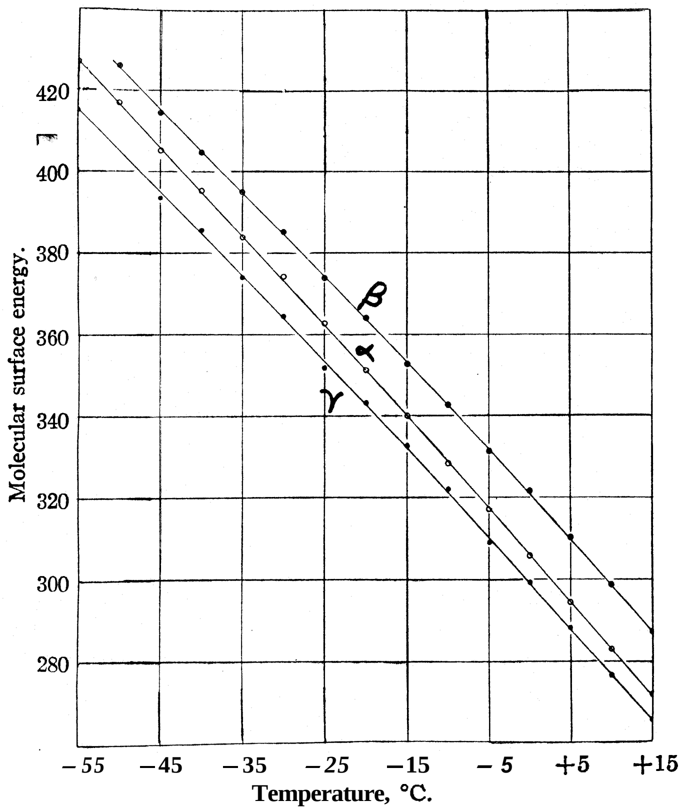
The physical properties of the butylenes and butanes together with those previously obtained by Maass and Wright for the two and three carbon compounds are compared in the following three tables. The melting points and critical temperatures of the butanes were taken from the literature.

TABLE IV

PHYSICAL PROPERTIES

Compound	M. p.	B. p.	Critical temp. Obs.	Critical temp. Calcd.	*Tb/Tc*
Ethane	−172.0	−88.3	35.0	34.6	0.60
Propane	−189.9	−44.5	95.6	91.6	.62
n-Butane	−135	−0.5	153.2	147.0	.64
***Iso*butane**	−145	−10.2	133.7	129.5	.64
Ethylene	−169.4	−103.9	9.9	5.9	.60
Propylene	−185.2	−47.0	92.1	91.3	.62
α-Butylene	<−190	−6.1	144	145	.64
β-Butylene	−127	1.0	155	156	.64
γ-Butylene	−146.8	−6.6	143.5	147	.64

The alternating melting point in the normal paraffin series is seen in the low melting point of propane as compared to ethane and normal butane. The olefins, with the rather surprising exception of a-butylene, have higher melting points than the corresponding paraffins. a-Butylene was not frozen, although kept for many hours with frequent agitation in the neighborhood of −210°. The liquid becomes very viscous but not glassy at this temperature,[6] and may be supercooled, but it is probable that its melting point is considerably below that of normal butane. The rule that the *iso* compound melts at a higher temperature than its straight chain isomer does not hold in the case of the butanes. The butylenes, however, follow this rule as well as that which states that the most symmetrical isomer has the highest melting point.



α = a-Butylene; β = β-butylene; y = y-butylene.

Fig. 4.

The *iso* compound in both cases is the more volatile, in agreement with the general rule. It is of interest to note that the ratio Tb/Tc has exactly the same value for all of the compounds containing the same number of

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[6] This substance, which is easily prepared pure, should make an excellent thermometric liquid for low temperature work.

carbon atoms. The critical temperature determined experimentally and the value calculated from surface tension data agree very well considering the relatively low temperatures at which the surface tensions were determined. The average value calculated differs by only −1.7° from that found.

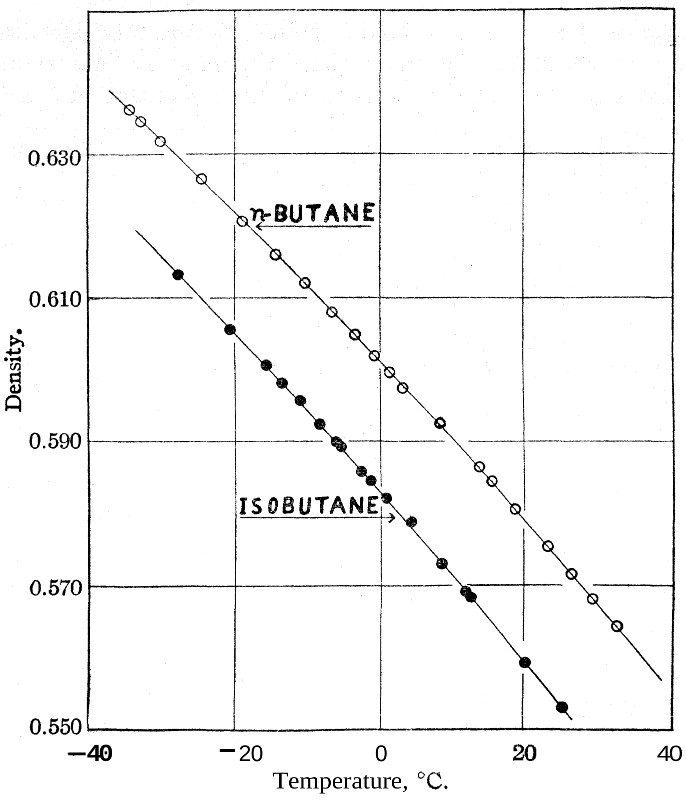

Fig. 5.

TABLE V

PHYSICAL PROPERTIES

Compound	Latent heat	Ramsay and Shields constant	Trouton's constant	Surface tension at the b. p.	Total surface energy
Ethane	3880	1.98	21.0	16.05	45.7
Propane	4700	2.15	20.6	15.63	50.3
n-Butane	5597	2.21	20.5	14.90	47.8
*Iso*butane	5480	2.23	20.8	14.10	47.2
Ethylene	3510	2.14	20.8	16.50	47.7
Propylene	4600	2.12	19.0	16.70	49.7
a-Butylene	5400	2.21	20.2	15.95	51.1
β-Butylene	5400	2.14	19.7	16.78	51.2
γ-Butylene	5200	2.15	19.7	15.72	49.8

The values for the Ramsay and Shields constant and for Trouton's constant show that all these liquids distinctly belong to the non-associated type. The molecular latent heats given were calculated from the vapor pressure data.

The surface tensions at the boiling point and the total surface energies show that unsaturation increases these properties. One would expect this from the greater polarity induced by the unsaturation. β-Butylene, the symmetrical compound, has a distinctly higher surface tension than either of its isomers. This is to be expected as is also the fact that the two *iso* compounds have lower surface tensions than their normal isomers. The total surface energies show no marked regularity and it is probable that only after the six-carbon compound will the constant value for the series be reached.

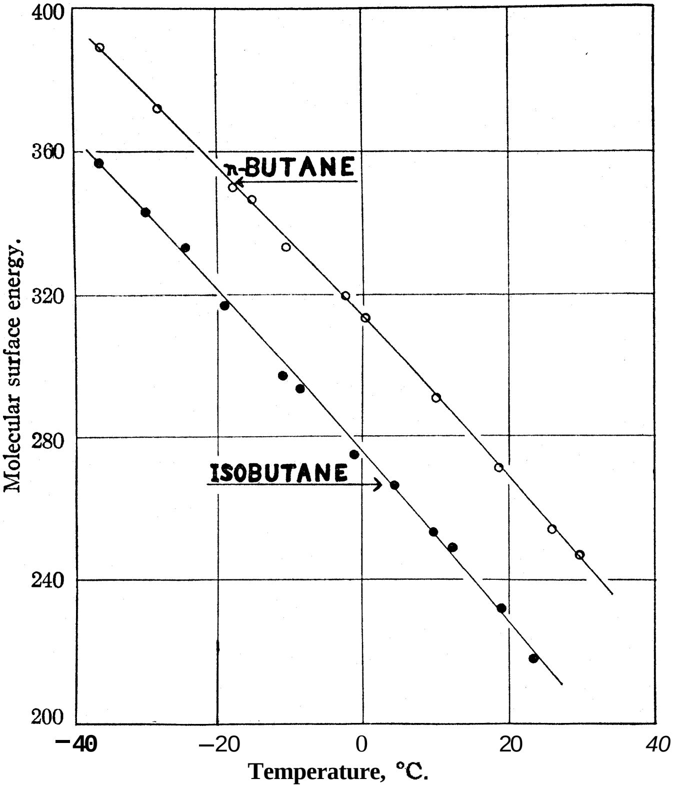

Fig. 6.

A comparison of the molecular volumes determined experimentally with those calculated on the basis of Kopp and Le Bas[7] shows that espe-

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[7] Le Bas, monograph, "The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green and Co., 1915.

TABLE VI

PHYSICAL PROPERTIES

Compound	Molecular volume at the b. p. Found	Molecular volume at the b. p. Calcd. Kopp	Molecular volume at the b. p. Calcd. Le Bas	Molecular volume at the m. p. Found	Molecular volume at the m. p. Calcd.
Ethane	54.9	55	51.6	32.8	41.6
Propane	75.0	77	73.7	41.3	59.4
n-Butane	96.3	99	95.9	76.0	77.2
*Iso*butane	97.6	99	95.9	78.1	77.2
Ethylene	49.1	45.5	44.2	32.4	35.6
Propylene	69.0	67.5	66.3	38.7	53.4
α-Butylene	89.5	89.5	87.8	..	71.2
β-Butylene	88.9	89.5	87.8	72.5	71.2
γ-Butylene	89.3	89.5	87.8	71.6	71.2

cially for the two- and three-carbon compounds, Kopp's values are in far better agreement. It is to be expected that Le Bas' values for the higher members should approach more nearly those of Kopp because he uses the same value for the CH_2 group. In the calculation of Kopp's values for the olefins, 1.5 units were added for unsaturation. This evidently was not enough for the first members. It is quite evident that Le Bas' contention that unsaturation does not cause an increase of volume cannot be maintained.

The values found by extrapolation for the molecular volume at the melting point and those calculated with Le Bas' figures are given in the last two columns of the above table. The four carbon compounds show fair agreement between the observed and calculated values but the others differ widely. The alternation emphasized by Le Bas is a simple consequence of the alternation of the melting points. The temperature coefficient of the density for the four carbon compounds is 0.0011 as compared to 0.0033 for the three and 0.0044 for the two carbon compounds.

Acknowledgment is made of a Bursary granted to one of us by the Research Council of Canada.

Summary

A number of the physical properties of the three butylenes and the two butanes have been accurately determined over a wide range of temperature. These quantities, together with those previously obtained for ethane and ethylene and propane and propylene, are discussed.

MONTREAL, CANADA

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, COLUMBIA UNIVERSITY, No. 566]

ESTERS OF FUROYLACETIC ACID

BY J. E. ZANETTI AND C. O. BECKMANN

RECEIVED JANUARY 13, 1928 PUBLISHED MAY 5, 1928

The properties and reactions of furoylacetic ethyl ester, first prepared by Bouveault,[1] were investigated by Torrey and one of us[2] and its close analogy to acetoaceticester and benzoylacetic ester were pointed out as well as some very decided differences in behavior, particularly in the stability of its oxime. The present paper deals with a further investigation of the methyl, n-propyl and n-butyl esters of furoylacetic acid.

Method of Preparation.—In the preparation of these esters the method first employed was the condensation of ethyl furoate with methyl, n-propyl and n-butyl acetates by metallic sodium. This method had to be abandoned owing to the violence of the reaction, which yielded unmanageable, tarry products and very small amounts of the esters. As Claisen[3] has shown, the active catalyst in the acetoacetic ester condensations is sodium ethylate, and when this method was employed the reaction ran smoothly and the yields reached 53% of the theoretical.

Properties of the Esters.—The esters are colorless, oily liquids except the n-butyl ester, which is a solid, m. p. 25". They have pleasant, aromatic odors and show the properties of keto-enol compounds, giving salts as well as oximes and semicarbazones. Attempts to prepare from them phenylhydrazones yielded in all cases the 1-phenyl-3-furyl-5-pyrazolone, which had been investigated by Torrey and one of us[2] in the study of derivatives of furoylacetic ethyl ester.

Behavior of the Oximes.—The fact that the oxime of furoylacetic ester was stable, whereas neither the benzoylacetic ethyl ester nor the acetoacetic ethyl ester gave stable oximes, was brought out and commented on at length by Torrey and one of us.[2] It was shown that the stability of the oxime could be accounted for by the theory of Abegg,[4] since the furfuryl group was more electropositive than either the phenyl or the methyl group and therefore would tend to produce a syn-oxime with respect to itself, diminishing the tendency of the compound to split off alcohol and pass into an isoxazolone. It was therefore of interest to determine whether the substituting alcohol group in the furoylacetic ester had any influence on the stability of the various oximes. Oximes with definite melting points were prepared from the methyl, n-propyl and n-butyl esters. Their melting points (heating rate 4° per minute, starting at room tem-

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[1] Bouveault, *Bull. soc. chim.*, [3] 25, 440 (1901).

[2] Torrey and Zanetti, Am. Chem. J., 44, 391 (1910).

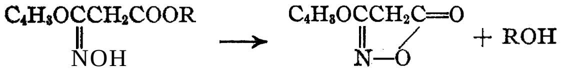
[3] Claisen, *Ann.*, 297, 92 (1897).

[4] Abegg, *Ber.*, 32, 291 (1899).

perature) were as follows: furoylacetic methyl ester oxime, 124–125°; furoylacetic ethyl[2] ester oxime, 131–132°; furoylacetic n-propyl ester oxime, 120–121°; furoylacetic n-butyl ester oxime, 101–102°.

It would be expected that the melting points of the oximes would increase with increasing molecular weight, and consequent rise in the boiling points of the esters, but this was not the case, as the n-butyl ester oxime melts nearly 30° below the ethyl ester oxime although the boiling point of the n-butyl ester under 3 mm. pressure is nearly 22° above that of the ethyl ester.

This unexpected behavior led to an investigation of what really happened when these oximes melted. Was the "melting point" a real melting point, that is, the passing of the solid oxime to the liquid phase, or a decomposition point where alcohol was split off and an isoxazolone formed? In the first case the liquid phase should solidify on cooling and the same melting point be obtained on remelting; in the second case either solidification should not be obtained or should be only partial and a different and lower melting point should be obtained. Experimental investigation disclosed that once melted, the oximes would only partially solidify and on redetermination of the melting point a much lower value was obtained. The obvious explanation was that alcohol was split off and that the second melting point was really the solution point of the isoxazolone in the alcohol formed according to the reaction



$$\mathrm{C_4H_3O\underset{\substack{\| \\ NOH}}{C}CH_2COOR} \longrightarrow \mathrm{C_4H_3O\underset{\substack{\| \\ N-O}}{C}CH_2C{=}O} + \mathrm{ROH}$$

It was then necessary to show that the isoxazolone was really formed at the "melting point." This was easily done by heating the oximes to their melting points in a small test-tube immersed in an oil-bath and lowering the pressure to cause the alcohol to boil off. In all cases needles of the furylisoxazolone sublimed to the cooler parts of the tube just above the level of the oil and showed the correct melting point for that compound, 147–148°. In the case of the methyl ester, the isoxazolone formation began considerably below the melting point, which can be explained by the much greater volatility of the alcohol formed.

In all these cases, then, the "melting points" are not true melting points but decomposition points and the point at which the liquid phase appears is determined by (1) the speed with which the formation of the isoxazolone takes place, and (2) the solution of the isoxazolone as well as of the undecomposed oxime in the alcohol formed.

Obviously these "melting points" are meaningless as criteria of purity unless the speed and time of heating are made constant. For example, the n-butyl ester oxime which melts at 102° when heated at the rate of 4 degrees per minute, starting at room temperature, will "melt" at 96° when held at that temperature for seven minutes, and when "dipped" at 98° will melt at 103°.

In explaining the fact that the oximes of these esters are stable, the position assigned by Hantzsch to the furyl group in his list of order for attraction for the OH group is inadequate if that order is followed in explaining the stability of the oximes of the acetoacetic ester homologs. It explains well enough why the benzoylacetic ester oxime should be unstable but falls down in the case of the furoylacetic ester oxime which according to him should be even less stable than that of the benzoylacetic ester. On the other hand, Abegg's theory explains the stability of the furoylacetic ester oximes but when his theory is applied to the higher esters it fails completely. According to him the n-propyl and n-butyl ester oximes should be *more* stable than the methyl and ethyl ester oximes, whereas the reverse has been shown to be the case, the n-propyl and *n*-butyl oximes splitting off the corresponding alcohols at *lower* temperatures than the methyl and ethyl oximes. There must be, therefore, some other factor than the electrostatic attraction for the OH group which comes into play in determining the stability of these oximes. It is not possible at present to decide on this matter.

TABLE I

DERIVATIVES OF THE ESTERS OF FUROYLACETIC ACID

	Sodium salt. Na, %		Potassium salt. K, %		Copper salt, Cu, %		Oxime			Semicarbazone		
Ester	Calcd.	Found	Calcd.	Found	Calcd.	Found	. p. C.	N, % Calcd.	Found	M. p. °C.	N, % Calcd.	Found
Methyl	12.10	12.00	18.97	18.64	16.00	16.14	....	7.65	7.78	....	18.66	18.43
	...	12.28	...	18.68	...	15.80	124–5[a]	..	7.48	141–2[a]	...	18.73
n-Propyl	10.55	10.19	...	...	14.02	14.33	....	6.63	6.60	....	16.60	16.80
	...	...	...	...	...	14.14	120–1[a]	..	6.76	137-k	..	16.34
n-Butyl	...	...	...	...	13.20	13.35	102[a]	6.22	6.21		15.73	15.49
	...	...	...	...	...	...	....	..	6.13	127–8[a]	...	16.01

[a] With decomposition.

Experimental

Methyl Ester of Furoylacetic Acid.—About 30 g. of sodium was placed in 500 cc. of dry xylene contained in a liter flask. To this was added the requisite amount of absolute alcohol to dissolve the sodium. The excess xylene was distilled off in a stream of hydrogen. The flask was then connected with a reflux condenser and a mixture of 75 g. of ethyl furoate and 140 g. of dry methyl acetate was added. The reaction mixture was heated on the water-bath for four to five hours. More dry methyl acetate was then added to keep the mixture liquid. The heating was continued for ten to twelve hours. The mixture was acidified with dilute acetic acid to liberate the ester. extracted with ether and dried with anhydrous sodium sulfate; the ether and the unchanged esters were distilled off and the ketonic ester was distilled under vacuum.

The ester is a colorless oil with a pleasant odor. It turns yellow on standing; b. p. 96–98' at 1 mm., 144–145° at 20 mm.; yield, 45–50% of the theoretical.

And. Calcd. for $C_8H_8O_4$: C, 57.14; H, 4.76. Found: C, 57.37, 57.26; H, 4.93, 4.76.

***n*-Propyl** Ester **of** Furoylacetic Acid.—The condensation of n-propyl acetate and ethyl furoate was carried out in the same manner as described for the methyl ester.

The ester is a colorless oil which turns yellow upon standing. It has a pleasant odor; b. p. 110–112° at 1 mm.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12. Found: C, 60.50, 60.67; H, 6.25, 6.13.

n-Butyl Ester of Furoylacetic Acid.—The condensation of n-butyl acetate and ethyl furoate was carried out in the same manner as described for the methyl ester. The ester is a colorless oil which turns yellow upon standing. It has a pleasant odor; b. p. 136–138° at 3 mm. On cooling it solidifies to white needles, m. p. 25.2°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.86; H, 6.66. Found: C, 62.80, 62.52; H, 6.66, 6.75.

Derivatives of the Esters of Furoylacetic Acid

Sodium Salts.—The sodium salts of the methyl and n-propyl esters were prepared by dissolving 1 g. of sodium in 25 cc. of absolute alcohol and adding the corresponding amount of the ester. In the case of the methyl ester the salt was so insoluble that it precipitated out in a few minutes. In the case of the n-propyl ester about one-half the alcohol had to be evaporated before crystallization occurred. The sodium salt of the butyl ester is evidently so soluble that we were unable to prepare it in a pure condition.

The sodium salts were recrystallized from alcohol and analyzed (see Table I). They are white, crystalline solids.

Potassium Salt.—An alcoholic KOH solution was added to the methyl ester. Upon standing for 3 to 4 hours, long white needles of the potassium salt separated out. They were filtered off and recrystallized from alcohol. They were soluble in water and hot alcohol and slightly soluble in ether. The potassium salts of the other esters could not be prepared in a pure condition owing to their much greater solubilities.

Copper Salts.—The copper salts were prepared by shaking an ether solution of the ester with a concentrated water solution of copper acetate. In the case of the butyl ester a benzene solution of the ester had to be used as the copper salt dissolves in ether and even slightly in benzene. The copper salts crystallized out in the form of small green needles. These were repeatedly washed with ether or benzene, dried and analyzed.

Oximes.—The oximes were prepared by mixing the theoretical amounts of hydroxylamine hydrochloride, sodium acetate and the esters in dilute alcohol, using just enough water to dissolve the hydroxylamine and just enough alcohol to dissolve the ester. The mixture was allowed to stand for four hours, when the oxime began to crystallize. About 4 to 5 volumes of water were then added, when a voluminous precipitate of the oxime would come out upon standing for another hour. The crystals were filtered, washed with water, dried and recrystallized from benzene. The oximes are white, fluffy crystals, soluble in alcohol, ether and hot benzene but insoluble in water. For melting points and analyses see Table I.

Semicarbazone.—The semicarbazones were prepared by mixing theoretical proportions of the esters, semicarbazide hydrochloride and sodium acetate. The rest of the procedure was the same as for the oxime. The semicarbazones were purified by recrystallization from a benzene-alcohol (3:1) mixture. The products were white, crystalline solids, soluble in alcohol, hot benzene and ether but insoluble in water. For melting points and analyses see Table I.

Summary

1. The methyl, n-propyl and n-butyl esters of furoylacetic acid, their typical salts, oximes and semicarbazones have been synthesized and their properties reported.

2. The stability of the oximes is discussed and shown to be contrary to Hantzsch's theory and not fully explained by Abegg's theory.

NEW YORK CITY

[CONTRIBUTION FROM BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

PREPARATION AND PROPERTIES OF THE 2-METHYL-5-ISOPROPYL PHENYL AMIDES OF SOME HIGHER FATTY ACIDS

BY RAYMOND M. HANN[1] AND GEORGE S. JAMIESON[2]

RECEIVED JANUARY 21, 1928 PUBLISHED MAY 6, 1928

The use of amides as a means of identification of acids is too generally recognized to require more than a passing mention. It is noteworthy, however, that the amides[3] of the higher fatty acids differ so slightly in melting point that it is questionable if the identification by this method is positive enough to be of much value. Phenyl amides and substituted phenyl amides show a greater increment between melting points of closely following members of the saturated series, but even here much is to be desired. Phenylene diamides have been prepared by De Conno,[4] and the differences in melting point between neighboring members of the series are of such magnitude as to be of use for differentiation.

It seemed possible that weighting of the phenyl nucleus and corresponding increase in the molecular weight would lead to some useful results. Accordingly cymidine (2 methyl-5-isopropylaniline) was prepared and coupled with the higher fatty acid chlorides. The resulting substituted phenyl amides were purified and their physical constants were determined. It was observed that up to arachidic acid the melting point of the amides increased with the molecular weight, but that arachidic and lignoceric cymidines are lower in melting point than myristyl cymidine. This condition finds an analogy in the behavior of the toluides, since palmitic toluide melts at 66, or 27° lower than myristic toluide, whereas in the phenylene diamides it has been observed that both stearic and arachidic *p*-phenylene diamides melt at lower temperatures than palmitic p-phenylene diamide.

Experimental

Cymidine was prepared from cymene by nitration according to Phillips'[5] modification of Andrews'[6] procedure and subsequent reduction by tin and

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[2] Chemist in charge, Oil, Fat and Wax Laboratory, Bureau of Chemistry and Soils, U. S. Department of Agriculture.

[3] Lewkowitsch and Warburton, sixth edition, Vol. I, p. 150.

[4] De Conno, *Gazz. chim. ital.*, 47, I, 93 (1917).

[5] Phillips, THIS JOURNAL, 44, 1777 (1922).

[6] Andrews, *J. Ind. Eng. Chem.*, 10, 453 (1918).

hydrochloric acid as directed by Wheeler and Smithey.[7] The acid chlorides were obtained from the pure acids and thionyl chloride as stated for lower homologs by Meyer,[8] except that the reaction period was increased by refluxing in an all-glass reaction vessel for one-half hour before distillation. Lauryl chloride boiled at 175–176°, under a pressure of 47 mm., myristyl chloride at 179–180° under 22 mm. and palmityl chloride at 199–200" under 20 mm. A high boiling residue was obtained in each case which contained some of the corresponding ketone.

The arachidic and lignoceric acids used in this study were separated from peanut oil in connection with the investigation of peanut oil.[9] The arachidic acid melted at 76–77°. *Anal.* Calcd. for $C_{20}H_{40}O_2$: H, 12.91; C, 76.85. Found: H, 12.90; C, 77.05. The lignoceric acid which melted at 80–85.5° gave by analysis: H, 13.01; C, 78.14. Calcd. for $C_{24}H_{48}O_2$: H, 13.13; C, 78.18.

Due to the limited quantity of these acids, the procedure adopted was to treat 3g. portions of the acids with an excess of thionyl chloride and after the reaction had taken place the excess of thionyl chloride was removed by distillation under reduced pressure. The reaction product, without purification, was used for the preparation of the derivatives.

The compounds described were all prepared by treating the acid chloride (3 g.) dissolved in ether with an excess of cymidine. An exothermic reaction took place and the condensation product separated gradually from the ether solution in crystalline condition. The solid was filtered off, worked with ether and recrystallized two or three times from alcohol. All were obtained as glistening white crystals which were soluble in alcohol, acetone and acetic acid. Table I gives the characteristics of each compound.

TABLE I

2-METHYL-5-ISOPROPYL AMIDES OF FATTY ACIDS

Amide of	Subs., g.	Analysis (KGA) 0.1 *N* HCl, cc.	N found, %	N calc., %	M. p., °C.
Lauric acid	0.1171	3.6	4.31	4.23	82–83
Myristic acid	.1056	2.8	3.71	3.69	88-89
Palmitic acid	.2062	5.4	3.67	3.44	90-91
Stearic acid	.1851	4.3	3.25	3.37	93–94
Arachidic acid	.1063	2.2	2.90	3.16	81–82
Lignoceric acid	.1097	2.2	2.81	2.97	84-85

Summary

The 2-methyl-5-*iso*propyl phenyl amides of lauric, myristic, palmitic, stearic, arachidic and lignoceric acids have been prepared and analyzed.

PITTSBURGH, PENNSYLVANIA

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[7] Wheeler and Smithey, THIS JOURNAL, 43,2613 (1921).

[8] Meyer, *Monatsh.*, 22, 417 (1901).

[9] Jamieson, Baughman and Brauns, THIS JOURNAL, 43, 1372 (1921).

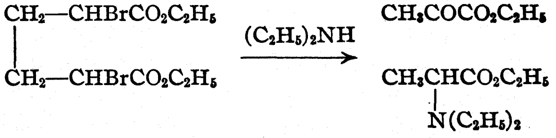
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE CLEAVAGE OF DIETHYL α,α'-DIBROMO-ADIPATE BY DIETHYLAMINE

BY REYNOLD C. FUSON

RECEIVED JANUARY 26, 1928 PUBLISHED MAY 5, 1928

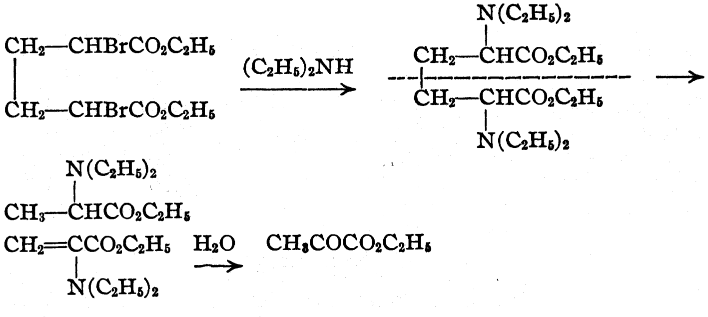
In a recent article von Braun, Leistner and Münch[1] described a remarkable and apparently novel type of rupture of an aliphatic carbon chain. Diethyl α,α'-dibromo-adipate on treatment with certain secondary amines does not yield the expected diamino-adipic esters but is severed into two three-carbon chains. Thus, in the case of diethylamine the products are ethyl pyruvate and an amino ester which was identified by von Braun and his co-workers as ethyl α-diethylaminopropionate.



$$\begin{array}{l} \mathrm{CH_2{-}CHBrCO_2C_2H_5} \\ | \\ \mathrm{CH_2{-}CHBrCO_2C_2H_5} \end{array} \xrightarrow{\mathrm{(C_2H_5)_2NH}} \begin{array}{l} \mathrm{CH_3COCO_2C_2H_5} \\ \\ \mathrm{CH_3CHCO_2C_2H_5} \\ \qquad | \\ \qquad \mathrm{N(C_2H_5)_2} \end{array}$$

It has further been shown that this type of reaction is peculiar to adipic esters. It does not take place when the corresponding dibromo esters of glutaric, pimelic and suberic acids are used.

The authors explain the chain decomposition by assuming replacement of the bromine atoms by amino groups and subsequent breaking down of the resulting diamino ester. Thus, when diethylamine is used it is assumed that diethyl α,α'-tetraethyldiamino-adipate is formed in the normal manner and that it then breaks down to form ethyl α-diethylaminopropionate and ethyl α-diethylamino-acrylate, the latter being hydrolyzed to ethyl pyruvate



$$\begin{array}{l} \mathrm{CH_2{-}CHBrCO_2C_2H_5} \\ | \\ \mathrm{CH_2{-}CHBrCO_2C_2H_5} \end{array} \xrightarrow{\mathrm{(C_2H_5)_2NH}} \begin{array}{l} \qquad \mathrm{N(C_2H_5)_2} \\ \qquad | \\ \mathrm{CH_2{-}CHCO_2C_2H_5} \\ \hline \mathrm{CH_2{-}CHCO_2C_2H_5} \\ \qquad | \\ \qquad \mathrm{N(C_2H_5)_2} \end{array} \longrightarrow$$

$$\begin{array}{l} \qquad \mathrm{N(C_2H_5)_2} \\ \qquad | \\ \mathrm{CH_3{-}CHCO_2C_2H_5} \\ \mathrm{CH_2{=}CCO_2C_2H_5} \\ \qquad | \\ \qquad \mathrm{N(C_2H_5)_2} \end{array} \xrightarrow{\mathrm{H_2O}} \mathrm{CH_3COCO_2C_2H_5}$$

To account for the breaking of the carbon chain an explanation based on space considerations is advanced. It is assumed that the adipic ester molecule is bent about as in I so that the two bromine atoms are held very close together in space.

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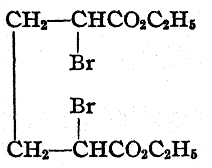
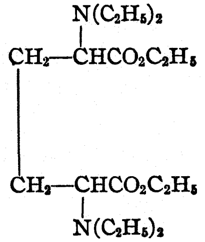
[1] Von Braun, Leistner and Münch, *Ber.*, 59B, *1950* (1926).



I

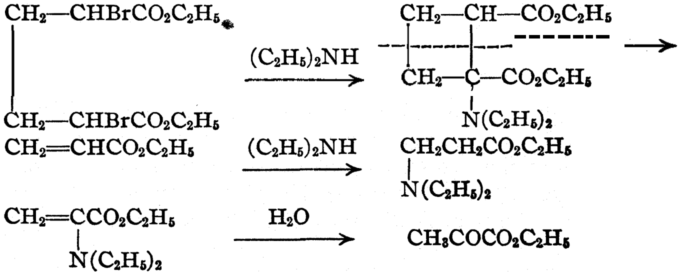


II

The exigency of space at this point in the molecule is assumed to be such that when the diethylamino groups are introduced they serve as a wedge, prying the ends of the molecule apart and rupturing the chain.

This mechanism is objectionable for several reasons. In the first place, diethyl α,α'-tetraethyldiamino-adipate when once formed is quite stable—a fact which cannot be explained on this theory. Furthermore, it seems unlikely that the bromine atoms or the diethylamino groups which replace them must necessarily lie near together as in I; they should be free to rotate and to occupy, for instance, the positions indicated in II if space factors demand it. It is hard to understand why substituents on the a-carbon atoms would prevent the free rotation of these atoms especially if the "preferred" position involves such internal stress in the molecule as would bring about its decomposition.

It is the object of the present article to show that the facts outlined above may be explained in another way—a way not only more completely in harmony with these facts but which identifies the apparently novel chain fission with a known type of reaction. It is postulated that a four-membered ring is formed as an intermediate and that this, in accordance with the well-known tendency of cyclobutane derivatives, dissociates into two molecules of ethylenic character.[2] Thus, again taking the diethylamine case as an example, the first step is the elimination of hydrobromic acid and the replacement of the second bromine atom by a diethylamino group to give diethyl 1-diethylamino-1,2-cyclobutanedicarboxylate. This compound then dissociates into ethyl acrylate and ethyl a-diethylamino-acrylate



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[2] Staudinger, *Ber.*, 44,526 (1911).

Ethyl a-diethylamino-acrylate like other amines of this general type should be easily hydrolyzed[3] and under the conditions of the experiment should appear as ethyl pyruvate, its hydrolysis product. This ester is actually obtained.

Ethyl acrylate, however, would not be expected to yield ethyl α-diethylaminopropionate—the other product reported by von Braun, Leistner and Munch. Flürscheim[4] has shown that in the presence of diethylamine and at a temperature of approximately 100°, ethyl acrylate is transformed quantitatively into ethyl 8-diethylaminopropionate. Under the conditions of the experiment, therefore, ethyl β-diethylaminopropionate should appear among the reaction products instead of the corresponding a-compound reported by von Braun and his collaborators.

An examination of the experimental work, however, reveals the fact that, although the amino ester in question was characterized by analysis and by the preparation of two derivatives, there is no evidence to show that it is the α- rather than the 8-ester. The work has, accordingly, been repeated and it has been shown that the amino ester obtained is really the β-isomer[5]—a result in accord with the reaction mechanism advanced in the present paper.

The identity of the amino ester was established by comparing it with authentic specimens of ethyl α-diethylaminopropionate and ethyl β-diethylaminopropionate. Both of these compounds are known, the former having been prepared by Flürscheim[4,6] and the latter by Adams and Dreger.[7] The following table gives the boiling points, densities, refractive indices and the melting points of the methyl iodide derivatives of the two known esters and of the unknown one.

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[3] Examples of this type of behavior are ethyl β-aminocrotonate [Geuther, *Z.* Chem., 7, **247 (1871)**], ethyl α-methyl-β-aminocrotonate [Conrad and Epstein, ***Ber.***, 20, **3056 (1887)**] and ethyl β-diethylaminocrotonate [Kuckert, ***Ber.*, 18, 619 (1885)**], all of which are more or less easily hydrolyzed to amines (or ammonia) and the corresponding esters.

β-Piperidinobenzalacetophenone [$C_6H_5COCH{=}C(NC_5H_{10})C_6H_5$] [André, Ann. *chim. phys.*, [8] **29,577 (1913)**] and a-piperidinobenzalacetophenone[$C_6H_5COC(NC_5H_{10}){=}CHC_6H_5$] [Watson, **J. *Chem. Soc.*, 85, 1322 (1904)**] are hydrolyzed at room temperature to give piperidine and the corresponding diketone [Dufraisse and Moureu, Bull. *soc.* ***chim.***, [4] **41,547** (1927)].

[4] Fliirscheim, **J. *prakt.*** Chem., **[2] *68*, 347 (1903).**

[5] It should be noted also that the alcohol obtained from this ester by reduction must be γ-diethylamino-*n*-propyl alcohol, $CH_2[N(C_2H_5)_2]CH_2CH_2OH$, and not β-diethylamino-n-propyl alcohol as reported by von Braun, Leistner and Münch.

Also, the compounds reported as ethyl α-di-*n*-propylaminopropionate, ethyl α-di-*iso*-amylaminopropionate, ethyl a-kopellidinopropionate and ethyl α-diethylamino-*n*-butyrate are presumably really the corresponding β-compounds. A report covering this point is in preparation.

[6] See also Gault, ***Bull. soc. chim.***, [4] **3, 376 (1908).**

[7] Adams and Dreger, unpublished work.

TABLE I

DATA ON ESTER DERIVATIVES

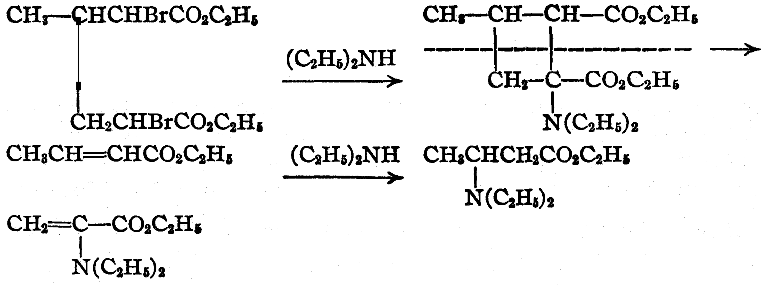
	α-Ester	β-Ester	Unknown
Boiling point	50–52°/3–4 mm.	63–65°/4 mm.	59–63°/3–4 mm.
Density at 20°	0.9077	0.9095	0.9097
n_D^{22}	1.4229	1.4266	1.4268
M. p. of CH_3I deriv.	....	80–81°	80–81°

The melting point of a mixture of the methyl iodide derivative of the β-ester and that of the unknown ester was 80–81°.

In order to determine whether ethyl α-diethylamino-acrylate was actually formed or not the decomposition was carried out in the normal way and the products were isolated without being allowed to come in contact with water or hydrochloric acid. In this way no ethyl pyruvate was obtained. The sole product was a liquid boiling at 76–82° (5–6 mm.) which is approximately the boiling point of pure ethyl β-diethylaminopropionate. It was suspected that this liquid was a mixture of ethyl β-diethylaminopropionate and ethyl α-diethylaminoacrylate. The high refractive index pointed to this conclusion.

Since it was not possible to separate the mixture by fractional distillation the whole was treated with dilute hydrochloric acid. From this reaction mixture were obtained not only pure ethyl β-diethylaminopropionate but ethyl pyruvate as well. This confirms the presence of ethyl α-diethylamino-acrylate as an intermediate.

The results obtained by von Braun and his associates with diethyl β-methyl-α,α'-dibromo-adipate serve to confirm the mechanism proposed here to explain the formation of the β-ester. In this case the reaction would be expected to take the following course, yielding ethyl crotonate in place of the ethyl acrylate postulated as an intermediate in the simpler case.



$$CH_3—\underset{|}{C}HCHBrCO_2C_2H_5 \; / \; CH_2CHBrCO_2C_2H_5 \xrightarrow{(C_2H_5)_2NH} CH_3—CH—CH—CO_2C_2H_5 \; / \; CH_2—\underset{N(C_2H_5)_2}{\underset{|}{C}}—CO_2C_2H_5 \longrightarrow$$

$$CH_3CH{=}CHCO_2C_2H_5 \xrightarrow{(C_2H_5)_2NH} CH_3\underset{N(C_2H_5)_2}{\underset{|}{C}}HCH_2CO_2C_2H_5$$

$$CH_2{=}\underset{N(C_2H_5)_2}{\underset{|}{C}}—CO_2C_2H_5$$

Here, however, the presence of the methyl group would be expected to retard the addition of diethylamine to the conjugated system. The isolation by the above-mentioned authors of *both* ethyl crotonate and ethyl β-diethylamino-*n*-butyrate is consistent with the above mechanism.

As a further confirmation of the mechanism given in this paper the stability of diethyl 1-diethylamino-1,2-cyclobutanedicarboxylate and similar cyclobutane derivatives is being studied.

Experimental Part

Meso-Diethyl α,α'-Dibromo-adipate and Diethylamine.—The procedure of von Braun. Leistner and Münch[8] was followed minutely; meso-diethyl α,α'-dibromo-adipate (m. p. 67°) was treated with three times the theoretical amount of diethylamine and the reaction products were worked up by treatment with ether and an excess of dilute hydrochloric acid. The neutral ester boiled at 155° at atmospheric pressure and formed a phenylhydrazone melting at 117–117.5'. The semicarbazone melted at 205°. A mixed melting point with the semicarbazone of an authentic specimen of ethyl pyruvate gave no depression.

The amino ester boiled at 59–63' (3 4 mm.); d^{B}, 0.9097; n_{D}^{22}, 1.4268. When heated at 100° with methyl iodide it gave a thick, brown sirup; this soon set to a mass of crystals which on recrystallization from ethyl acetate melted at 80–81°. A mixed melting point with the methyl iodide derivative of an authentic specimen (see below) of ethyl β-diethylaminopropionate gave no depression.

The Preparation of Ethyl β-Diethylpropionate

This ester was prepared from ethyl β-bromopropionate according to the procedure, of Flürscheim.[4] The ethyl β-bromopropionate, which was made from ethylene cyanohydrin,[9] was treated with diethylamine in the following way.

Seventy-three grams (1.0 mole) of diethylamine was added slowly to 90 g. (0.5 mole) of ethyl β-bromopropionate. The reaction was vigorous at the beginning but slowed down at the end of about thirty minutes. The mixture was then made up largely of crystals of diethylamine hydrobromide and was heated for an hour on the steam-bath. After being allowed to cool it was taken up in ether and an excess of dilute hydrochloric acid. The ether layer was removed and the aqueous layer was made alkaline with potassium hydroxide. The amino ester which separated as an oil was removed by extraction with ether. The ether solution was dried over anhydrous potassium carbonate and distilled. The ester came over at 63–65° (4 mm.); d^{20}, 0.9095; n_{D}^{22}, 1.4266.

Contrary to the experience of Fliirscheim, ethyl 8-diethylaminopropionate cannot be distilled undecomposed at atmospheric pressure. At its boiling point (190–195°) it decomposes slowly to give diethylamine and ethyl acrylate.

The Preparation of Ethyl a-Diethylaminopropionate

The procedure of Adams and Dreger[7] was used. Twenty-three grams of ethyl α-bromopropionate was treated with 92 g. of diethylamine and the amino ester was isolated in the manner described above for the corresponding @-compound. It boiled at 178–183° (1 atm.); 50–52° (3 4 mm.); d^{B}. 0.9077; n_{D}^{22}, 1.4228. Attempts to prepare a methyl iodide derivative yielded an oil which did not crystallize.

Meso-Diethyl α,α'-Dibromo-adipate and Diethylamine (Second Procedure)

Thirty grams of meso-diethyl α,α'-dibromo-adipate (m. p. 67°) was treated with 37 g. of diethylamine in the manner described by von Braun, Leistner and Münch.[10]

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[8] Ref. 1, p. 1953.

[9] Kendall and MacKenzie, "Organic Syntheses," John Wiey and Sons, Inc., New York, 3, 25 (1923).

[10] Ref. 1, p. 1953.

When the reaction was complete, the white crystalline solid, diethylamine hydrobromide, was filtered off, dried and weighed. The yield was practically theoretical.

The liquid product (filtrate) was distilled with a column. After the diethylamine was distilled off the product passed over at 90–100° (21 mm.). A considerable dark-colored residue remained in the flask. On redistillation the liquid boiled at 76–82° (5–6 mm.); n_D^{24}, 1.4385. There was again a dark-colored residue.

This redistilled product was shaken with dilute hydrochloric acid and the mixture, after being allowed to stand for an hour, was extracted with ether. The ether extract when dried and distilled yielded a liquid boiling at 155° which formed a phenylhydrazone melting at 117–117.5°. A mixed melting point with the phenylhydrazone of ethyl pyruvate gave no depression.

The aqueous layer was made alkaline and extracted with ether. The dried ether extract was found on distillation to contain a liquid boiling at 63–65° (4 mm.) which formed a methyl iodide derivative melting at 80–81°. By the method of mixed melting points this compound was identified as the methyl iodide derivative of ethyl β-diethylaminopropionate.

Summary

When diethyl α,α′-dibromo-adipate is treated with an excess of diethylamine the products are ethyl pyruvate and ethyl β-diethylaminopropionate.

It has been shown that ethyl α-diethylamino-acrylate is probably an intermediate in the formation of the pyruvic ester.

A mechanism involving the intermediate formation of a cyclobutane ring is suggested to explain these results.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYTIC OXIDATION WITH AIR OF ETHYL, ISOPROPYL AND n-BUTYL ALCOHOLS

BY ROBERT M. SIMINGTON[1] AND HOMER ADKINS

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In seeking information as to the role played by the catalyst in the oxidation of alcohols by air an extended experimental study has been made as to the relative amounts of reaction products obtained by the oxidation of ethyl, *iso*propyl and *n*-butyl alcohols over some 30 catalysts. The products of oxidation are carbon dioxide, carbon monoxide, saturated and unsaturated hydrocarbons, hydrogen, an aldehyde or ketone and an acid and its ester. The relative amounts of these products are determined by the nature of the alcohol, the alcohol–air ratio, and the chemical and physical properties of the catalyst.[2]

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[1] The authors are indebted to the E. I. DuPont de Nemours Co. for the support of a fellowship enjoyed by Dr. Simington during the academic year 1926–27.

[2] Orloff, J. *Russ. Phys.-Chem. Soc.*, 40, 203 (1908), *C. A.*, 2, 3346 (1908); also a footnote by Gibbs on p. 93 of Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922.

The apparatus used is shown in the figure. Air from a compressed air line was passed through the alcohol, which had been dried by refluxing three times over lime. The outlet tube from the flask containing the alcohol was electrically heated to prevent the condensation of alcohol. The alcohol–air mixture was passed over the catalyst supported in the quartz tube C by means of a quartz rod. The catalyst tube was half a meter in length and had an internal diameter of seven millimeters. The catalyst was heated to the desired temperature by an electric furnace eleven centimeters in length, the temperature of which was controlled by means of a potentiometer temperature controller. In most cases the heat of reaction was sufficient to keep the catalyst at a red heat after the reaction had begun.

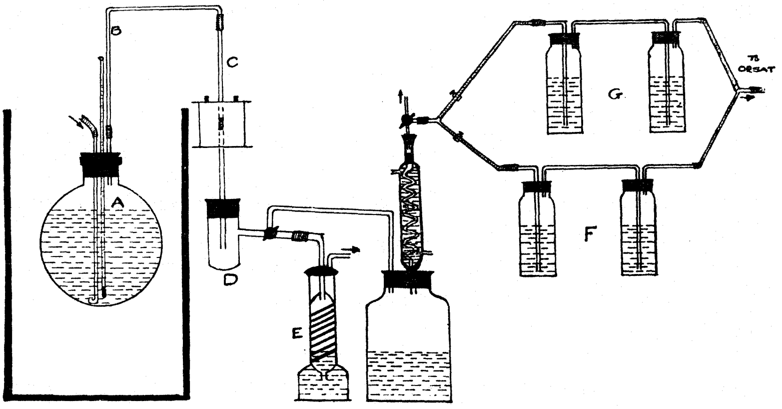

Fig. 1

The gases from the reaction tube were passed through the tube D, which was heated by means of an electric hot-plate to prevent any liquid from condensing out of the gas stream. By means of a three-way stopcock attached to the tube D, the gas stream could be led either through the special wash bottles E, for aldehyde or ketone and acid determinations, or into the gas analysis apparatus, after passing through the cooling system and two wash bottles containing concentrated sulfuric acid or sodium bisulfite.

The acid was determined by allowing the gas to flow for eight minutes through the wash bottle E containing about two hundred cubic centimeters of water. The total sample was titrated with standard base and the amount of acid calculated.

Immediately after the acid determination another wash bottle containing exactly two hundred cubic centimeters of a 3% solution of sodium bisulfite was attached and the gases passed through for two minutes. The concentration of the bisulfite solution was determined by adding to an aliquot an excess of iodine and back-titrating with standard sodium thiosulfate. After the aldehyde was collected, a 10cc. aliquot of the bisulfite solution was titrated in a similar manner. The difference between the two titrations is a measure of the aldehyde or ketone present, since one molecule of sodium bisulfite combines with one molecule of aldehyde or ketone. In the ketone determination an excess of sodium bisulfite amounting to three or four times that needed was added and both the blank and run were permitted to stand for thirty hours as recommended by Jolles.[3]

A 100-cc. sample of gas was drawn during an interval of two to three minutes in order to obtain a uniform sample. The gases from the catalyst were washed through concentrated sulfuric acid G before all analyses except those for alkenes. Since concentrated sulfuric acid combines with or polymerizes alkenes, the gases were washed through sodium bisulfite F to remove the aldehyde or ketone for these determinations. Since the sodium bisulfite evolved sulfur dioxide, these samples could not be used for carbon dioxide determinations. The carbon dioxide was absorbed in potassium hydroxide, the unsaturated hydrocarbons in bromine water, the oxygen by phosphorus and the carbon monoxide by an acid solution of cuprous chloride. The hydrogen was estimated by contraction during combustion and the saturated hydrocarbon by absorption of carbon dioxide after combustion.

The amount of alcohol passed over the catalyst per hour was determined by weighing the flask **A** before and after the run. The rate of air flow was shown by a calibrated flowmeter and the pressure by a mercury manometer.

Copper and silver were used as the basic metals. Various forms of catalysts such as gauze, pellets, strips and wire were tried but no noticeable variations were found. The following were the chief catalysts used:

(1) Copper gauze; (2) copper wire; (3) brass plated on copper gauze; (4) 10% copper, 90% silver; (5) 50% copper, 50% silver; (6) 90% copper, 10% zinc; (7) 80% copper, 20% zinc; (8) 50% copper, 50% zinc; (9) 97.5% copper, 2.5% bismuth; (10) 90% copper, 10% cadmium; (11) 99% copper, 1% palladium; (12) 99% copper, 1% gold; (13) 99% copper, 1% platinum; (14) 99% copper, 1% nickel; (15) 50% copper, 50% nickel; (16) 50% copper, 50% manganese; (17) 90% copper, 10% silicon; (18) silver gauze; (19) silver pellets from Merck's precipitated silver and also from the reduction of ammoniacal silver nitrate with formaldehyde; (20) 99% silver, 1% gold; (21) 99% silver, 1% zinc; (22) 99% silver, 1% bismuth; (23) 99% silver, 1% palladium; (24) platinum gauze; (25) nickel gauze; (26) 50% copper oxide, 50% molybdenum oxide; (27) 50% copper oxide, 50% uranium oxide; (28) 50% copper oxide, 50% iron oxide; (29) 50% copper oxide, 50% vanadium oxide; (30) 50% copper oxide, 50% tungsten oxide.

The alloys were made by melting the two constituents together in a porcelain or graphite crucible for fifteen to thirty minutes, pouring into water and cutting into the desired size. The oxide mixtures were prepared by grinding the various oxides with copper oxide in a mortar and molding into pellets. Brass, copper and silver were

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[3] Jolles, Ber., 39, 1306 (1906).

plated on nickel and copper gauzes but gave unsatisfactory results because the high temperature caused the plated metal to diffuse quite rapidly into the base. The amount of catalyst used varied from two to six grams, depending upon its volume.

Space is not available to publish more than a small fraction of the data available, so that only a summary of the more significant experiments is given in the tables. The air flow in the experiments whose results are reported below was **83** (0°, 760 mm.) liters per hour, this flow being chosen because it gave the most satisfactory results in the preliminary runs. The figures of the gas analyses in Tables I and II are those taken after the analysis showed that a constant value had been reached. This was usually three or four hours after the oxidation was started. The figures in Col. C_1 represent the contraction due to the combustiom of the mixtures of hydrogen and hydrocarbons. It is thought advisable to report the contraction instead of assuming a certain hydrocarbon to be present. The figures under C_2 represent the contraction in volume which took place on absorption of carbon dioxide formed in the combustion. Table I shows the best yields of aldehyde or ketone obtained. The data from runs in which the 0.8 mole of alcohol per hour was passed over various catalysts have been collected in Table II. The figures under "A" represent the amount of alcohol in moles passed over the catalyst per hour. The figures under "B" represent the number of moles of alcohols converted to the

TABLE I

THE MAXIMUM YIELD OF ALDEHYDES AND KETONES

Catalyst	A	B	C	CO_2	C=C	Ot	CO	C_1	C_2	%
				Ethyl Alcohol						
Cu 90%, Ag 10%	1.31	0.98	0.016	3.7	..	1.9	0	2.3	1.2	76.0
				Isopropyl Alcohol						
Silver pellets	0.755	0.572	0.006	6.0	0.8	3.0	1.1	3.1	1.8	76.1
				n-Butyl Alcohol						
Copper 80%, Zinc 20%	0.811	0.586	0.015	5.6	1.2	3.6	1.4	2.8	1.8	72.5
Silver pellets	0.60	0.43	0.012	7.5	..	3.8	0.0	4.8	3.0	72.0

TABLE II

OXIDATION OF ALCOHOLS OVER VARIOUS CATALYSTS

Alcohol"	A	B	C	CO_2	C=C	O_2	CO	C_1	C_2	%
				Copper Gauze						
Ethyl	0.80	0.298	0.014	6.8	0.2	0.8	3.8	5.0	3.0	37.4
*Iso*propyl	.82	.404	.007	5.2	0.0	7.0	1.0	1.6	1.4	49.0
	.83	.416	.023	5.8	0.9	2.7	3.0	5.6	3.8	50.2
Butyl	.84	.482	.012	4.6	2.4	5.0	2.8	4.6	2.5	57.4
				Silver Gauze						
Ethyl	.82	.356	.017	6.2	0.0	3.0	2.8	3.5	2.0	43.7
*Iso*propyl	.79	.512	.006	6.2	0.6	4.6	1.4	0.8	0.4	64.6
Butyl	.80	.544	.015	4.0	2.4	5.4	2.6	3.3	1.0	68.3

TABLE II (*Concluded*)

Alcohol[a]	A	B	C	CO_2	$C=C$	O_2	CO	C_1	C_2	%
Copper 90%, Zinc 10%										
Ethyl	.79	.395	.016	8.3	0.2	1.2	2.0	9.2	3.1	51.6
Isopropyl	.80	.494	.008	7.7	0.6	1.2	1.8	5.3	1.8	61.5
Butyl	.831	.575	.015	5.8	1.8	2.4	2.0	3.4	2.4	69.1
Copper 80%, Zinc 20%										
Ethyl	.80	.248	.016	7.8	0.4	5.0	2.2	13.8	1.3	31.0
*Iso*propyl	.78	.532	.010	7.4	0.6	1.9	1.8	6.5	1.3	67.8
Butyl	.81	.586	.015	5.6	1.2	3.6	1.4	2.8	1.8	72.5
Copper 50%, Zinc 50%										
Ethyl	.80	.253	.020	8.3	0.8	3.8	3.5	26.8	2.4	33.0
*Iso*propyl	.80	.347	.029	6.4	2.2	2.2	3.4	14.0	2.0	43.5
Butyl	.77	.494	.010	6.2	1.5	5.0	1.4	12.0	1.5	63.9
Copper 97.570, Bismuth 2.5%										
Ethyl	.82	.419	.012	8.0	0.2	1.0	2.5	4.0	1.8	51.0
Isopropyl	.77	.395	.007	7.1	0.2	2.4	2.0	2.0	1.4	51.5
Butyl	.80	.507	.006	5.0	5.4	1.2	4.4	10.1	6.3	63.6
Manganese 50%, Copper 50%										
Ethyl	.80	.286	.016	7.7	1.5	1.5	4.0	8.8	2.0	33.6
Isopropyl	.83	.195	.007	8.2	0.8	3.2	2.4	4.4	0.4	23.6
Butyl	.83	.371	.007	6.2	4.0	2.4	3.2	8.8	4.0	44.8
Copper Oxide 50%, Vanadium Pentoxide 50%										
Ethyl	.81	.240	.002	1.0	0.6	15.0	2.0	0.8	0.7	29.9
Isopropyl	.80	.082	.002	0.8	11.4	16.6	0.0	0.2	0.0	10.4
Butyl	.80	.223	.004	1.8	2.0	13.8	0.0	2.0	1.8	28.1
Copper Oxide 50%, Molybdenum Oxide 50%										
Ethyl	.80	.111		1.6	0.2	15.0	0.0	1.0	0.5	13.7
*Iso*propyl	.79	.120	.00	0.6	10.0	16.4	0.0	0.2	0.0	15.2
Butyl	.80	.315	.002	0.2	2.2	16.4	0.0	1.2	1.2	39.3
Copper Oxide 50%, Tungsten Oxide 50%										
Ethyl	.81	.193	.002	0.9	2.1	10.6	4.4	4.6	2.4	23.9
*Iso*propyl	.78	.167	.003	1.4	5.4	15.2	0.2	0.4	0.4	21.5
Butyl	.	.422	.005	1.2	6.8	10.0	0.4	4.2	3.8	50.5
Copper Oxide 50%, Uranium Oxide 50%										
Ethyl	.81	.177	.008	7.8	1.0	3.4	2.8	8.8	1.8	21.9
*Iso*propyl	.81	.217	.010	8.4	1.4	3.6	2.4	4.4	0.4	26.3
Butyl	.82	.411	.008	6.2	5.4	1.2	2.2	10.2	6.4	50.0
Nickel 1%, Copper 99%										
Ethyl	.80	.354	.018	7.1	0.0	1.6	3.0	2.8	1.8	43.7
*Iso*propyl	.80	.397	.007	7.2	1.0	1.4	2.8	3.0	2.1	49.8

[a] Ethyl alcohol was held at 46°, *isopropyl* alcohol at 41° and butyl alcohol at 80° in these experiments, the pressure being about 50 mm. above that of the atmosphere.

corresponding aldehyde or ketone per hour. The figures under "C" represent the number of moles of alcohol converted to acid, acetic acid being assumed to be formed from ethyl and isopropyl alcohols and butyric acid from butyl alcohol. The figures given in the last column of the table represent the percentage conversion of alcohol to aldehyde or ketone. The percentage yields would be increased if account were taken of the alcohol that did not react. A much more efficient oxidation of an alcohol may be attained if the percentage of alcohol entering into reaction is low. Catalysts 4 and 18 with ethyl, 5 and 22 with isopropyl and 2 and 18 with butyl alcohol gave better than a 70% yield of aldehyde or ketone.

The results as shown in Table II indicate that approximately three molecules of ethyl alcohol and two of isopropyl alcohol to one of butyl alcohol break down to form carbon dioxide. This ratio is independent of the kind of metal catalyst and of the mixed oxide catalysts which remained hot during the reaction. Those oxide catalysts which had to be externally heated—vanadium, tungsten and molybdenum—do not show this ratio.

Butyl alcohol produced more unsaturated hydrocarbons with the metallic catalysts than either ethyl or isopropyl alcohol. With the copper oxide–molybdenum oxide, copper oxide–vanadium oxide and copper oxide and tungsten oxide catalysts, isopropyl alcohol produced 10.0%, 5.4% and 11.4% of unsaturated hydrocarbon, respectively, while with the same catalysts under the same conditions of alcohol flow ethyl alcohol produced 0.2, 2.1 and 0.2%, respectively, and butyl alcohol 2.2, 5.4 and 2.0%, respectively.

That zinc brings about an increase in the production of hydrogen is shown by the fact that the contractions reported in column "C_1" increase very appreciably as the content of zinc is increased. This effect is most marked with ethyl alcohol and least with butyl alcohol, which indicates that under these conditions ethyl alcohol is more easily dehydrogenated than isopropyl or butyl alcohol.

Constable[4] has shown that there are practically no active points which cause dehydrogenation on the surface of copper gauze, foil, hammered or plated copper at temperatures above 400°. It is therefore probable that in our experiments the surface is being almost continuously reactivated. That a change of surface does take place is shown by the fact that a copper catalyst after use may vary from a golden yellow to black color. This color is due to a very thin layer of material, which is presumably an oxide.

If only a relatively few points on a catalyst be active, then these should be easily poisoned or their character changed by the addition of small amounts of foreign materials. Pease[5] has shown that 200 mg. of mercury per 100 g. of catalyst reduced the adsorption of hydrogen to $^1/_{20}$ of its former value. Mercury in much larger amounts than those described by Pease

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[4] Constable. *Proc. Roy. Soc. (London)*, **110A**, 283 (1926).

[5] Pease, This Journal, **45**, 1196 (1923).

was found to have no deleterious effects on the catalytic oxidation of alcohols. Lazier (unpublished data) has found that 1% of nickel in a copper catalyst produced a very marked effect in the dehydrogenation of ethyl alcohol but no appreciable differences were found when this catalyst was used for oxidation. Alloys of silver and of copper containing 1% of gold, platinum, palladium, nickel or bismuth did not differ markedly from the pure silver or copper. Larger amounts of material incorporated in the catalyst produced marked differences, as shown by the increase in hydrogen content of the gases with increase of the zinc content of the catalysts. Fifty per cent. of nickel incorporated into a copper catalyst caused a rapid decomposition with a heavy deposition of carbon. Ten per cent. of silicon in copper inhibited the reaction almost completely.

Several of the oxide mixtures differed from the alloys in the products formed and their relative amounts. The catalyst containing 50% of molybdenum oxide produced very noticeable amounts of formaldehyde from all three alcohols. The tungsten oxide-copper oxide mixture also produced formaldehyde but to a lesser extent. The oxide mixtures containing vanadium, tungsten and molybdenum oxides did not cause sufficient oxidation to maintain incandescence and had to be heated externally. The oxide mixtures of copper and iron and copper and uranium did not require external heating.

Summary and Conclusions

Ethyl, isopropyl and butyl alcohols have been mixed with air and passed over a number of catalysts with the production of aldehyde or ketone, acid, carbon dioxide, carbon monoxide, saturated and unsaturated hydrocarbons and hydrogen. The oxidation of butyl alcohol resulted in the formation of a small amount of ester with all catalysts and some formaldehyde with the mixed oxide catalysts. The following catalysts were used during the investigation: silver, nickel, copper and platinum gauzes; copper wire, silver pellets, pellets of alloys of copper and zinc, nickel, bismuth, palladium, platinum, gold and manganese, and silver alloys of copper palladium, platinum, gold and bismuth. Oxide mixtures of uranium and copper, tungsten and copper, molybdenum and copper, vanadium and iron and copper have been used. Silver and silver–copper alloys produced better than 70% yields of aldehyde or ketone. Ethyl alcohol has been found to produce approximately three times as much carbon dioxide as butyl alcohol and twice as much as isopropyl alcohol.

The amount of hydrogen in the effluent gases was found to be small except when brasses were used as catalysts. Large amounts of zinc apparently promote dehydrogenation but not oxidation of the hydrogen. Butyl alcohol was found to produce more unsaturated hydrocarbons than either ethyl or isopropyl alcohol except with oxide catalysts, which caused the production of 10 to 15% of unsaturated compounds with *iso*propyl alcohol. This latter fact indicates that the oxide catalysts were not completely reduced to the metals. The production of saturated hydrocarbons is rather small in all other cases. Acid production was found to be small and fairly constant for the same alcohols over different catalysts.

The plated catalysts were found to be unsatisfactory because the high temperature of reaction apparently caused solution of the plated metal into the supporting metal. It also seems likely that the reaction takes place throughout the catalyst. Evidence for this view is found in the change in mechanical properties of the gauzes, wire and pellets, and in the reduction of copper oxide to metallic copper in the center of pellets of a copper oxide–vanadium oxide mixture.

The temperature of the reaction varied with the alcoholair ratios and with the catalysts employed. The copper–vanadium, copper–molybdenum and copper–tungsten oxide mixtures were comparatively inactive and external heating was necessary. Heat was also applied to maintain a reaction at the surface of the 50% zinc-copper alloy,

The fact that small amounts of material incorporated into the metallic catalysts produce no marked effect indicates that a larger portion of the surface of the catalyst is active in the catalytic oxidation of alcohols.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

THE ADDITION OF SODIUM MALONIC ESTER TO ALIPHATIC MUSTARD OILS

BY DAVID E. WORRALL

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Phenylisothiocyanate reacts smoothly with substances containing an active methylene group, such as malonic ester, acetoacetic ester and acetylacetone, forming sulfur derivatives that have been shown[1] to be useful for the preparation of heterocyclics of the isoxazole and pyrazole series. Similar transformations might be expected starting with methylisothiocyanate; accordingly, with the hope of extending the scope of these reactions so as to include the aliphatic mustard oils, work has been resumed on the chemistry of the isothiocyanates. It first became necessary to synthesize the desired thio-amides, for methyl mustard oil, which is far more expensive and more difficult to prepare than phenyl mustard oil, has been much less studied. No such work has been done with it. This communication deals with the action of several alkyl mustard oils on dimethyl and diethyl malonate.

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[1] Worrall, THIS JOURNAL, 42, 1055 (1920); 44, 1551 (1922); 45, 3092 (1923); 46, 2832 (1924).

Sodium diethyl malonate and methyl mustard oil react as follows.

$$NaCH(COOC_2H_5)_2 + CH_3NCS = CH(COOC_2H_5)_2C(SNa)NCH_3$$

The product is soluble in cold water, from which it is precipitated by the addition of hydrochloric acid.

$$CH(COOC_2H_5)_2C(SNa)NCH_3 + HCl = NaCl + CH(COOC_2H_5)_2C(SH)NCH_3$$
$$CH(COOC_2H_5)_2C(SH)NCH_3 = CH(COOC_2H_5)_2CSNHCH_3$$

The last equation is reversible, for the thio-amide is soluble in aqueous alkali. Therefore, carbethoxy ethylmalonate monothiomethylamide is a typical tautomeric substance existing in the form of an equilibrium mixture.

Similar products were obtained with ethyl, propyl, butyl, amyl and benzyl mustard oils. The yields were excellent in all cases, approximately 80% of the theoretical as a rule. In one instance the crude product accounted for 87% of the material used. These thio-amides are oils or low-melting solids, insoluble of course in water but very easily dissolved by organic solvents. Because oils difficult to purify were formed in most cases, dimethylmalonate was substituted for the ordinary ester and, as expected, solid addition products were obtained. The yields were not as good as with diethyl malonate, for greater difficulty was experienced in obtaining a complete reaction between sodium and the methyl ester.

These addition products behave exactly as one would expect of malonic ester derivatives. Complete decomposition is induced by heating with water containing either acid or alkali.

$$CH(COOC_2H_5)_2CSNHCH_3 + 4H_2O = CH_3COOH + 2CO_2 + H_2S + CH_3NH_2 + 2C_2H_5OH$$

With cold aqueous sodium hydroxide it is possible to obtain one of the intermediate products, malonic acid monothiomethylamide. It is formed as the result of the loss of carbon dioxide as well as hydrolysis.

$$CH(COOC_2H_5)_2CSNHCH_3 + 2H_2O = CH(COOH)_2CSNHCH_3$$
$$CH(COOH)_2CSNHCH_3 = CO_2 + CH_2(COOH)CSNHCH_3$$

These transformations take place at low temperatures and in alkaline solution, for hydrated sodium carbonate crystallizes out when concentrated solutions are used.

The substances actually isolated are not the free acids but sodium salts, although in the procedure first used the alkaline solutions of the thio-amides were decomposed with an excess of dilute hydrochloric acid. The fact that the sodium salts are alkaline toward phenolphthalein in water solution led to the discovery that sodium is present and not water of crystallization, an assumption that first suggested itself as the explanation of the low results observed on an examination of the analytical data for sulfur. The lower members of this series of salts are very soluble in water and quite insoluble in most organic solvents. Hence a very welcome observation was their solubility in acetone, which is an admirable vehicle for isolating them. It is not miscible in water containing alkali and so the sodium hydroxide solution of the thio-amides may be extracted directly with warm acetone. On cooling, the substances separate out as lustrous, irregular, plate-like crystals. The butyl and amyl derivatives are sufficiently sparingly soluble in cold water to permit the use of this solvent, although acetone is much the superior solvent. These salts are very hygroscopic and must be kept in a desiccator before analysis. Decomposition takes place on heating, with blackening and evolution of carbon dioxide. The free acids were not isolated, neither was the sodium salt of malonic acid monothiomethylamide, the first member of the series.

Malonic acid monothiobenzylamide, in marked contrast to the other amides, is precipitated from alkaline solution as the free acid by the addition of hydrochloric acid. It dissolves less readily in aqueous alkali than the other amides and is only sparingly soluble in water, from which it may be recrystallized. It loses carbon dioxide on heating, thereby changing smoothly into thio-acetyl benzylamide.

$$CH_2(COOH)CSNHCH_2C_6H_5 = CO_2 + CH_3CSNHCH_2C_6H_5$$

In this respect it acts like the corresponding derivatives obtained from the aromatic mustard oils. All of these sulfur derivatives have a bitter taste and react quickly with silver nitrate, forming silver sulfide.

Experimental

The mustard oils, except methyl and ethyl which can be purchased, were prepared by the method of Delépine,[2] in which a primary amine in water solution is brought in contact with carbon bisulfide and sodium hydroxide. Lead nitrate, substituted for lead acetate, was added to the mixture, which was then steam distilled. The yields of redistilled product varied from 50 to 75% of the theoretical. Sodium malonic ester was prepared in dry ether by the action of pulverized sodium. The preparation always contained metallic sodium even after long heating under a reflux condenser. Usually 10 g. of the ester was converted into the sodium derivative, after which the molar equivalent of the mustard oil was added and the mixture heated under a reflux condenser for several hours. The ester gradually changed into a heavy, compact white powder and the mixture showed a strong tendency to bump. It was then cooled and poured into water containing crushed ice. Any unchanged sodium present rose to the top and gradually disappeared in the moist ether layer without any danger of taking fire. Another advantage of having the ether present is that it extracts all organic impurities from the water layer except sodium malonic ester. The aqueous layer was then separated and acidified with an excess of dilute hydrochloric acid. An oil always formed but on standing for a few minutes it usually became solid. It was purified by dissolving in a small amount of warm alcohol and then adding water until the solution just missed becoming turbid.

The monothio-amides of malonic acid were obtained by dissolving the original addition product in 20% sodium hydroxide solution, using two or three times the equivalent amount of alkali and allowing the mixture to stand in a cool place overnight. Then by shaking with warm acetone and evaporating to a small bulk, the desired substance was quickly obtained in a relatively pure condition. The yields were only fair and an examination of the aqueous residue always revealed some of the original

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[2] Delépine, *Bull. soc. chim.*, [4] 3, 642 (1908).

thio-amide unchanged. Some hydrogen sulfide was also set free on the addition of a mineral acid, so it was evident that some of the material had entirely gone to pieces.

Malonic acid monothiobenzylamide was isolated by adding an excess of hydrochloric acid to the alkaline solution, filtering and recrystallizing the precipitate from warm water. In the analyses for sulfur the substances were heated to 225–250° for at least twenty hours with fuming nitric acid.

TABLE I

THIO-AMIDES

Of Carbethoxy Ethylmalonate

Name, Carbethoxy ethylmalonate monothio-	Formula	M. p., °C.	Decomp., "C.	Cryst. form	Sulfur analysis Calcd., %	Sulfur analysis Found, %
Methylamide	$C_9H_{15}O_4NS$	49–50	.....	Narrow plates	13.6	13.9
Ethylamide	$C_{10}H_{17}O_4NS$	51–52	.....	Needles	13.0	13.2
Propylamide"	$C_{11}H_{19}O_4NS$	11 (approx.)	.....	Needles	..	..
Butylamide[b]	$C_{12}H_{21}O_4NS$	Oil	.....	....	11.6	12.2
		Of Carbethoxy Methylmalonate				
Csrbethoxy methylmalonate monothio-						
Propylamide	$C_9H_{15}O_4NS$	4243	.....	Flat needles	13.8	14.1
Butylamide	$C_{10}H_{17}O_4NS$	62-63	.....	Needles	12.9	13.0
Amylamide	$C_{11}H_{19}O_4NS$	52–53	.....	Needles	12.2	12.5
		Of Malonic Acid				
Malonic acid monothio-						
Ethylamide	$C_5H_8O_2NSNa$	....	148–149	Plates	(Na, 13.6)	(Na, 13.4)
Propylamide	$C_6H_{10}O_2NSNa$	....	155–156	Plates	17.5	17.7
Butylamide	$C_7H_{12}O_2NSNa$	....	156–157	Plates	16.2	16.2
Amylamide	$C_8H_{14}O_2NSNa$	....	157–158	Plates	15.2	15.4
Benzylamide[c]	$C_{10}H_{11}O_2NS$	95–96	.....	Plates	15.3	15.3
		Of Acetic Acid				
Thio-acetyl benzylamide	$C_9H_{11}NS$	62-63	.....	Needles	19.4	19.5

[a] M. P. taken of crude subst. in water.

[b] Oil became crystalline in freezing mixture. Crude subst. analyzed,

[c] CO_2 evolved on melting.

Summary

Methyl, ethyl, propyl, butyl, amyl and benzyl mustard oils form addition products with sodium dimethyl and diethyl malonates.

These addition products in alkaline solution change into the sodium salts of malonic acid monothio-amides.

Under similar conditions the benzyl derivative forms the free acid. It loses carbon dioxide when heated to the melting point, changing into thio-acetylbenzylamide.

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[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 172]

THE SYNTHESIS OF 1-BUTENE[1]

BY HOWARD J. LUCAS[2] AND ROBERT T. DILLON[3]

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Introduction

The preparation of 1-butene has been carried out in the following ways: (a) the action of zinc diethyl upon vinyl bromide,[4] (b) the action of zinc dimethyl upon allyl iodide,[5] (c) the catalytic dehydration of 1-butanol over aluminum phosphate,[6] aluminum oxide[6c] zinc chloride[7] and (d) the action of alcoholic potash upon 1-bromobutane.[8] Its formation has also been observed in the dehydration of 2-butanol over zinc chloride[9] and of 2-methyl-2-propanol over aluminum phosphate.[6a] In addition two other methods appear feasible: (e) the action of zinc upon 1,2-dibromobutane in a manner similar to the preparation of 2-pentene,[10] and (f) the action of methylmagnesium iodide upon allyl bromide, similar to the preparation of higher 1-alkenes.[10,11]

To each of the first methods certain objections can be raised, namely: in (a) and (b) the presence of the zinc halide in the reaction mixture is objectionable, since zinc salts are known to cause, at high temperatures, a shifting of double bonds; in (c) the dehydration of the alcohol leads to the production of more than one hydrocarbon; in (d) the yields are poor, due to the formation of an ether and in *(e)* pure 1,2-dibromobutane is best obtained from bromine and pure 1-butene. It seemed reasonable to assume that the method (f) would yield the purest product, provided the hydrocarbon could be removed from the reaction mixture as soon as formed.

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[1] This paper contains the results of one phase of an investigation on the "Preparation of Pure Typical Hydrocarbons and a Study of Their Behavior When Heated Alone and with Catalysts" listed as Project 14 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund 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] Director, Project 14.

[3] American Petroleum Institute Research Fellow.

[4] Wurtz, Ann., 152, 22 (1869).

[5] Wurtz, Ann., 144, 234 (1867).

[6] (a) Senderens, Compt. rend., **144**, 1110 (1907); (b) Bull. *soc.* chim., (4) 1, 689 (1907); (c) Lépingle, *ibid.*, **39**, 741 (1926).

[7] LeBel and Greene, *Compt.* rend., **89**, 413 (1879).

[8] (a) Lieben and Rossi, Ann., 158, 164 (1871); (b) Grabowsky and Saizew, Ann., 179, 330 (1875); (c) Michael and Brunel, *Am.* Chem. *Jour.*, **41**, 118 (1909).

[9] Ipatiev and Sdzsitovecki, J. Russ. *Phys.-Chem.* Soc., 39, 897 (1907).

[10] Kirrmann, Bull. *soc.* chim., **39**, 988 (1926).

[11] (a) Brooks and Humphrey, THIS JOURNAL, 40, 822 (1918); (b) Norris and Joubert, *ibid.*, **49**, 873 (1927).

The synthesis of 1-butene from methylmagnesium iodide and allyi bromide takes place according to the reaction

$$CH_2{=}CH{-}CH_2Br + CH_3MgI \longrightarrow CH_2{=}CH{-}CH_2{-}CH_3 + MgIBr$$

In carrying out this operation it was thought best to modify the original procedure[11a] in which the allyl bromide is added slowly to the ethereal solution of the Grignard reagent since first the temperature of the solution is not sufficiently high for a rapid reaction, second the hydrocarbon has a high solubility in the ether from which its separation is more or less difficult, and third the removal of the product as soon as it is formed is desirable in order to reduce to a minimum the possibility of isomeric change. Accordingly as much of the ether as possible was driven out by heating the ethereal solution of the magnesium compound in an oil-bath to 130°, after which the temperature of the bath was dropped to 70° and held there while the allyl bromide was added with constant stirring. The butene was generated immediately at a rate corresponding to the rapidity with which the bromide was added.

The purification of the hydrocarbon required the removal of the ether, allyl bromide and methyl iodide, Considerable amounts of ether were carried by the gas even after cooling to about 5°, while the amounts of the halides were much less. The high solubility of butene in methyl and ethyl alcohols, more especially in the latter, precludes the use of these two substances as wash liquids, although when diluted by water to a strength of about 30% they will remove some ether and alkyl halide. In one experiment 30% methyl alcohol effected a fair removal of these materials. It was found that perchloric acid in water has markedly different solvent powers toward ether and toward butene; for example, a 37% solution dissolves approximately two and one half times its own volume of ether on mixing, while it absorbs only 15% of its volume of gaseous 1-butene. The perchloric acid solution is thus a more satisfactory wash liquid than the dilute alcohol. However, some of the higher boiling impurities pass through and condense out with the butene, the final purification of which may be accomplished by fractional distillation through an efficient column cooled to −15° to −18°. Purification by fractional distillation through a cooled column is preferable to repeated distillations from one flask directly into another. The run-back from the column is at all times fairly large and the separation from higher boiling material is satisfactory.

Experimental

Preparation of 1-Butene.—The Grignard reagent was prepared in the three-necked, 3-liter flask (A, Fig. 1) in the usual manner from 51 g. (2.1 moles) of magnesium turnings, 300 g. (4.0 moles) of absolute ether and 284 g. (2.0 moles) of methyl iodide, b. p. 41.5–0.6° at 744 mm. The contents were agitated by the mercury sealed stirrer B and the ether was refluxed back by the bulb condenser C.[12] Stirring was continued for some time after the iodide had been added and the resulting material allowed to stand overnight in an atmosphere of nitrogen. The next day the liquid was carefully decanted from the unchanged magnesium into a flask similar to A. This was connected to the apparatus, a condenser was attached for down distillation and the flask was heated rapidly in an oil-bath with stirring until the temperature of the bath reached 130". When the rate with which the ether distilled became slow a stream of nitrogen was passed into the flask,[13] the heating was discontinued and the flask was attached to the absorbing train as shown in Fig. 1. As soon as the bath temperature dropped to 70°, *232* g. (1.92 moles) of allyl bromide, b. p. 69–70' C.,[14] was introduced slowly through the dropping funnel D with stirring. The gas, which was evolved at once,[15] passed through the bulb condenser C cooled by water at 5°, next through four glass-stoppered wash bottles E of 200cc. capacity, the first containing 30% methyl alcohol and the other three containing 100 cc. of 37% perchloric acid to remove ether, then through a tower F filled to about three-fourths of its capacity with anhydrous calcium chloride and one-fourth with soda lime and finally into G, surrounded by a Dewar flask filled with a cooling bath below −15°.[16] The butene which condensed out in G was purified by fractional distillation (see Fig. 2).

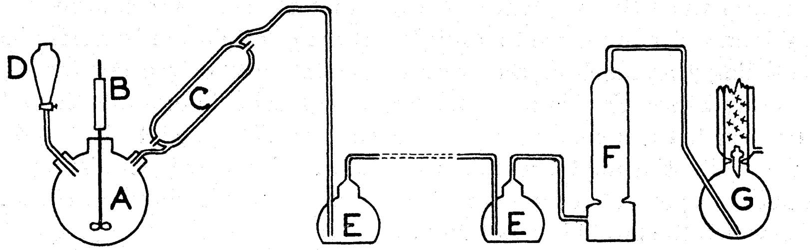

Fig. 1.—Apparatus for preparation and purification of 1-butene; A, reaction flask, *3* liter; *B,* mercury sealed stirrer; C, bulb condenser; D, dropping funnel; E, four wash bottles; F, drying tower: G, distilling flask, kept at −15 to −25°.

Fractional Distillation of 1-Butene.—As soon as the generation of the hydrocarbon was over, a flow of salt solution at −15 to −17° was started through the jacket H (Fig. *2*). *G* was now warmed by water first at 0 to +5° and later at higher tempera-

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[12] The inner water-containing bulb of the condenser C was 24 cm. long and 7.3 cm. in diameter, and had therefore a condensing surface of 550 sq. cm. This is equivalent to the condensing surface of a Liebig condenser the inner tube of which has an inside diameter of 1.0 cm. and the jacket of which is 175 cm. long. The distance between the inner and outer walls was made small, 3 mm. in fact, in order to have a small gas space. This is desirable when the condenser is used in a gas stream as the loss of gas for obvious reasons is minimized.

[13] After removal of the ether the Grignard reagent is a thick, viscous mass and readily absorbs oxygen and carbon dioxide. An inert atmosphere is desirable.

[14] The allyl bromide was prepared from allyl alcohol (b. p. 80–95°), sodium bromide and sulfuric acid by the method described in "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 15. The bromide was twice fractionally distilled.

[15] An excess of allyl bromide is indicated by immediate cessation of gas evolution.

[16] Suitable cooling baths are alcohol–solid carbon dioxide, ice–60% sulfuric acid and ice-concentrated hydrochloric acid mixtures.

tures. As the butene boiled it refluxed from the fractionating column of 5 × 5 mm. cut-glass rings in the tube I. This column, which was 22 cm. long and 2.5 cm. in diameter, was supported by the hollow glass nipple J.[17] The thermometer K graduated in $^1/_{10}$ degree registered the temperature of the gas at the top of the column. The gas was further purified by passing it through four wash bottles L, one containing 30% methyl alcohol to remove organic halides and three containing 37% perchloric acid to remove ether and methyl alcohol, next through a tower M containing soda lime and calcium chloride and finally into N, similar in construction to *G* and kept below −15°. The gas was again fractionally distilled from N and sealed off in suitable tubes. When 30% methyl alcohol was used as the wash liquid instead of perchloric acid, the product was distilled between the temperature ranges of −6.6 to −6.3° and −6.8 to −6.5' at 748 mm. in the first and second distillations, respectively. In the experiment in which perchloric acid was the wash liquid the temperature recorded during the first distillation was high due to the fact that the thermometer bulb was so far up in the apparatus that liquid was not condensing upon it. In the second distillation the range was −6.7 to −6.5°. The difference in the character of the residues remaining after these distillations indicates that perchloric acid removes impurities from the butene better than does dilute methyl alcohol. The time taken for the preparation, starting with the heating of the Grignard reagent, was about eighteen hours. This could be shortened considerably by using a more efficient purifying train since a more rapid flow of gas would then be possible. The yield is about 43 g. or 40% of the theoretical. The smallness of the yield may be ascribed in part to the fact that in the interest of purity a considerable amount of butene was discarded at the beginning and at the end of the distillations.

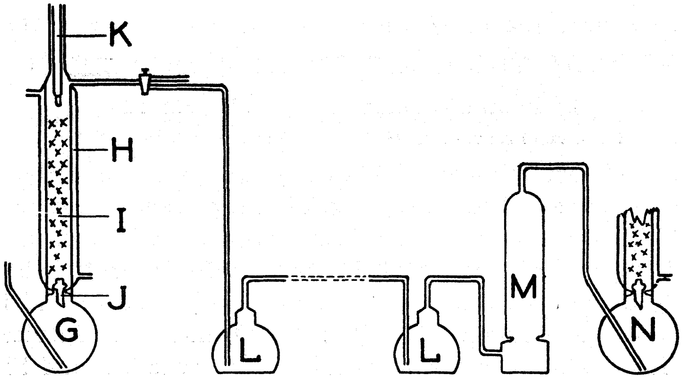

Fig. 2.—Apparatus for distillation of 1-butene; G, distilling flask, 300 cc.; H, jacket, for circulation of brine at −15 to −17°; I, column of cut glass rings; J, hollow glass nipple; K, thermometer, graduated in 1/10'; L, four wash bottles; M, drying tower; N, distilling flask, similar to G.

The absence of 2-butene in the final product is indicated by the purity of the dibromide obtained by the addition of bromine at −5 to −10°. The dibromide was fractionally distilled through a column of cut-glass rings which was 70 cm. long, 2 cm. in diameter, and surrounded on the outside by a packing of mineral wool 6 cm. thick. This column had previously served for the separation of a mixture of 1,2- and 2.3-dibromo-

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[17] Lucas, *Ind. Eng. Chem.*, 19, 680 (1927).

butanes. The dibromide from the synthetic 1-butene distilled almost entirely at 80.5–80.7° under 50.0 mm. and gave no indication that 2,3-dibromobutane was present. Its refractive index, n_D^{20}, was 1.5171. These constants were unaffected by subsequent distillation.

Summary

The hydrocarbon, 1-butene, is conveniently and rapidly prepared by adding allyl bromide to methylmagnesium bromide at 70° with stirring. The Grignard reagent should be previously heated in a bath at 130° in order to remove as much ether as possible. Dilute perchloric acid is effective in removing ether from the gas stream.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY]

EQUILIBRIUM IN THE REACTION $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$[1]

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It has been shown by Sabatier[4] that the hydrogenation of carbon dioxide to produce methane and steam is effected in the presence of catalytic nickel at 200–350°. By employing the free energy equations of Lewis and Randall,[5] it may be calculated that the reverse reaction, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, should proceed to the extent of 28.6% at 500° and 1 atmosphere, using a stoichiometric ($1\ CH_4 : 2\ H_2O$) mixture. In view of the fact that little data are available on this reverse reaction, and that *a* determination of the position of equilibrium allows of an independent calculation of the free energy of methane, which is at present based solely on dissociation experiments conducted chiefly at high temperatures (1200–1600°), some further study of the reaction seemed desirable. We have, therefore, carried out both forward and reverse reactions at 500° and have determined the equilibrium position at this temperature. Since the result is in excellent agreement with the value calculated from the Lewis and Randall equations, we have considered that further work was unnecessary. This report deals with the above mentioned measurements.

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[1] This paper reports the results of an investigation carried out as a part of Project No. 7 of the American Petroleum Institute research. Financial assistance in this work has been received from the research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

We wish to acknowledge also the assistance and advice of Professor Hugh S. Taylor of Princeton University, who is Director of Project No. 7. The title of this project is "Catalytic Methods Applied to Petroleum Hydrocarbons."

[2] Research Associate, American Petroleum Institute.

[3] Research Assistant, American Petroleum Institute.

[4] Sabatier and Senderens, *Comfit. rend.*, 134, 689 (1902).

[5] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. 485, 571, 576.

Experimental Method

The flow method was employed. Methane and steam, or carbon dioxide and hydrogen, or mixtures of the four were passed at known rates of flow over a supported nickel–thoria catalyst at 505°, and the off-gas was measured and analyzed.

Calibrated flowmeters regulated the rates of flow of methane, carbon dioxide and hydrogen. These gases passed into a mixing chamber containing calcium chloride and the mixture then entered the heated catalyst tube. Steam was introduced as follows. Into the top of a 50 cc. buret was sealed a small dropping funnel, the stem of which was drawn out to a fine capillary. On the side of the buret near the top a capillary was sealed and bent downward. This capillary was joined at right angles to the tube conveying the gases to the catalyst and met the latter close to the furnace, at which point a plug of glass wool was introduced. Water was displaced from the buret at a constant rate by a fine stream of mercury flowing at constant head from the dropping funnel. The displaced water was taken up by the glass wool in the tube leading to the catalyst and was vaporized into the gas stream by the heat of the furnace. The furnace was tilted slightly to facilitate the passage of the liquid water.

The effluent gas was passed through weighed tubes of calcium chloride and of "askarite" (a form of soda lime) for absorption and determination of water vapor and carbon dioxide, respectively. To prevent condensation of water between the furnace and the calcium chloride tube, a small evaporating dish was placed directly under the connecting tube and gently heated. A thermometer in contact with the tube was kept at 100°. The unabsorbed gases were then collected over a 50% glycerine–water mixture in a 2-liter aspirator bottle. Hydrogen, carbon monoxide, methane and nitrogen were determined by fractional combustion with copper oxide. The total volume of this gas was measured in a gas buret.

The furnace consisted of a 30-inch length of steel tubing, 4 inches in diameter, set in a sheet-iron jacket about 1 foot in diameter. The latter was packed with loose magnesia. The steel tube was wound with heavy asbestos covered nichrome wire. The catalyst bulb occupied the middle fifth of this tube, the ends of which were packed with magnesia and blocked with asbestos disks.

Temperatures were measured with a chromel-alumel thermocouple set in a Pyrex tube in contact with the catalyst bulb. The couple was calibrated by taking the eutectic point (517.1°) of a mixture of 55% of sodium sulfate and 45% of potassium chloride.

In making a run the furnace was brought to temperature and the desired mixture passed through for at least one hour to ensure obtaining a steady state. The weighed absorption tubes were then connected to the aspirator bottle. Connection with the outlet tube of the catalyst bulb was then made and the time taken. The gas flow was then controlled by means of a stopcock through which the confining liquid in the aspirator bottle escaped to a receiver. The flowmeters were by this means kept at the proper mark. Considerable care was taken to maintain the flow and to hold the current through the furnace constant throughout the run.

The gases were of high purity. They were analyzed with the following results: methane—CH_4, 97.2%; N_2, 2.8%; hydrogen—H_2, 97.5%; N_2, 2.2%; O_2, 0.3%; carbon dioxide—CO_2, 99.4%; N_2, 0.6%.

In our earlier runs the catalyst was found to be slowly losing activity. We attributed this to traces of sulfur compounds in the methane and thereafter passed this gas over hot copper granules heated to 300–400°, with the result that no further poisoning was noted.

The rates of flow were of the order of 100–200 cc. per minute, and the apparent volume of the catalyst was about 100 cc. The space velocities were, therefore, of the order of 1 to 2 cc. of gas per cc. of catalyst per minute.

The catalyst was prepared by impregnating diatomite brick (10–20 mesh) with a solution of nickel nitrate and thorium nitrate. Twelve and five-tenths g. of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.5 g. of $Th(NO_3)_4$ were dissolved in water and the solution made up to 15 cc. This was allowed to fall drop by drop on 25 g. of the brick. The latter was then placed in the catalyst bulb, and dried and reduced in a current of hydrogen in the furnace. The temperature was slowly raised to 350° over several hours.

Results

The results of our measurements are given in Table I. We have calculated the volumes in liters of gases flowing into the system at 25° and 1 atm. from the flowmeter settings and the times (20 minutes) of the runs. (The volume of liquid water as read on the buret was converted to liters of vapor under these conditions.) These are given for comparison with the volumes of effluent gases. Under ideal conditions the volume, for example, of methane and carbon dioxide passed in should equal the volume of methane, carbon dioxide and carbon monoxide issuing from the system. Actually there is usually some discrepancy. This is doubtless in part due to temperature and pressure corrections to be applied to the flowmeters. It is also due to errors in the measurement and analysis of the off-gas.

TABLE I

EQUILIBRIUM MEASUREMENTS AT 505°

Temp., °C.	Press., mm Hg.	Liters influent gas at 25°, 1 atm.					Liters effluent gas at 25°, 1 atm.						$K_{atm.} = \frac{[CO_2][H_2]^4P^2}{[CH_4][H_2O]^2}$
		CH_4	H_2O	CO_2	H_2	N_2	CH_4	H_2O	CO_2	H_2	CO	N_2	
Methane and Steam Only													
506	758.8	0.91	1.80	..	..	0.03	0.65	0.9	0.205	0.940	0.050	0.015	0.04
506	761.0	.97	1.95	..	..	.03	.73	.7	.180	.840	.040	.040	.04
506	785.2	.93	1.95	..	..	.03	.675	.6	.185	.820	.035	.040	.06
Carbon Dioxide and Hydrogen Only													
503	748.8	..	..	0.84	3.36	.07	.495	1.0	.290	1.030	.045	.020	.07
506	738.0	..	..	.82	3.27	.07	.505	1.0	.280	1.040	.045	,020	.07
Mixture Corresponding to 15% Conversion of Methane													
503	767.0	.72	1.40	.13	.50	.03	.505	1.45	.245	1.130	.040	,050	.033
608	744.5	.67	1.35	.12	.47	.03	.445	1.55	.260	1.160	.040	.025	.036
Mixture Corresponding to 45% Conversion of Methane													
502	761.8	.49	1.00	.40	1.59	.05	.535	1.40	.270	1.080	.035	,045	.030
505	766.0	.49	1.00	.40	1.59	.05	.515	1.45	.285	1.160	.040	.030	.046
Mixture Corresponding to 30% Conversion of Methane													
503	772.1	.62	1.25	.27	1.09	.04	.510	1.45	.300	1.130	.040	.050	.038
505	766.0	.59	1.20	.26	1.03	.04	.505	145	.280	1.140	.035	.040	.039
Accepted value[a] of $K_{atm.}$ =													.037

[a] The equilibrium constants were calculated from the mole fractions of gases and their total pressure in atmospheres. Mole fractions were calculated from liters of the individual gases in the effluent and the total number of liters. The pressure represents the observed atmospheric pressure in millimeters divided by 760.

In the early runs there was some difficulty over the determination of the amount of water in the off-gas, due to condensation. Accordingly, only one significant figure is given for the first five runs. For the remainder of the runs, we believe that the composition of the off-gas is known to about 1%.

In the first three runs methane and steam only were introduced. Analysis of the off-gas revealed that 20–25% of the methane was converted to carbon dioxide. The next two runs were made with carbon dioxide and hydrogen only. These showed that 35–37% of the carbon dioxide was unchanged. These results indicated that equilibrium corresponded to the conversion of between 20 and 40% of the methane to carbon dioxide when stoichiometric mixtures were employed. Accordingly, three sets of two runs each were carried out, in the first of which a mixture corresponding to 15% conversion of methane was introduced, in the second a mixture corresponding to 45% conversion and in the third a mixture corresponding to 30% conversion. Equilibrium constants calculated from the results of these six runs all gave substantially the same result. We take the average—0.037—as our value at 505°, the average temperature of the runs.

The numerical value of the constant $K_{\text{atm.}} = [CO_2][H_2]^4P^2/[CH_4][H_2O]^2$ is highly sensitive to variations in the proportions of the gases. Thus a variation of 1% in the percentage of methane converted causes a 20% change in the value of K. Hence high precision in the latter is not to be expected. The extreme variations from our average value of 0.037 are 0.030 and 0.046, corresponding to a discrepancy of something like ± 2% in the determination of the equilibrium ratio. We take this to be our extreme experimental error.

We may compare our results with that calculated from the Lewis and Randall free energy equations already referred to. The latter give for the reaction, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, $\Delta F = 37010 - 7.88T \ln T - 0.00475T^2 + 0.000000105T^3 + 14.42T$. For $T = 778°$ K. (505°), $\Delta F_{778} = 5030$ cals., whence $\log K_{\text{atm.}} = \dfrac{\Delta F}{4.579T} - 8.5880^{-10}$; and $K_{\text{atm.}} = 0.0387$. This value is in excellent agreement with our value of 0.037. We may therefore feel assured that the Lewis and Randall equations are adequate for the calculation of the equilibrium in this reaction at temperatures in the neighborhood of 500°. We may also conclude that the equation which these authors give for the free energy of methane expresses that quantity satisfactorily in the neighborhood of 500°. There was some question about this point since in this range the equation depended on data on the dissociation of methane into carbon and hydrogen in the presence of a nickel catalyst. Uncertainty arises as to the form-of the deposited carbon.

It will be noted that we have reported in Table I quantities of carbon monoxide of the order of 1% in the effluent gas. This may be formed by the reaction, $CH_4 + H_2O \rightleftarrows CO + 3H_2$, or by the reaction, $CO_2 + H_2$ $CO + H_2O$. Calculations based on Lewis and Randall's free energy data show that the equilibrium constant for the first reaction is 0.00539 at 500°, and that the effluent gas from our experiments should contain 1.3% of carbon monoxide at 1 atm. total pressure. This is of the order of the amount obtained. The water-gas equilibrium has an equilibrium constant of 0.989 at 500°. This corresponds to a carbon monoxide concentration of 0.6% in the effluent gas from our experiments, which is somewhat less than was obtained.

In treating of experiments with methane and steam at 500° and above, it will in general be necessary to take account of the three reactions, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, CH4 + $H_2O \rightleftarrows CO + 3H_2$ and $CO_2 + H_2 \rightleftarrows CO + H_2O$. There is no necessity that all these reactions shall take place under a given set of conditions, nor that the composition of off-gas shall be predictable from the equilibria in the above reactions. It is not unlikely, however, that with a catalyst such as we have used, and at temperatures of 500° and above, the off-gas will approximate to a composition which will satisfy all three reactions. For convenient reference we have tabulated below in Table II the equilibrium constants at 500, 600 and 700" for these reactions.

TABLE II

CALCULATED EQUILIBRIUM CONSTANTS

I—$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$; II—$CH_4 + H_2O \rightleftarrows CO + 3H_2$; III—$CO_2 + H_2 \rightleftarrows CO + H_2O$

Temp., °C.	Reaction I	Reaction II	Reaction III
500	0.0325	0.00539	0.0989
600	0.949	0.0696	.1983
700	15.06	11.03	.339

It is of interest to consider the reactions between methane and steam as a possible source of hydrogen. If carbon dioxide is formed, four volumes of hydrogen are obtained for every volume of methane reacting, while if carbon monoxide is formed, three volumes of hydrogen are obtained. Removal of water and carbon dioxide leaves a gas rich in hydrogen and containing as impurities methane and carbon monoxide. For example, a mixture of one volume of methane and two volumes of steam gives at 500" under equilibrium conditions a gas containing 40% of steam, 32% of hydrogen, 20% of methane, 8% of carbon dioxide and 1% of carbon monoxide. On removal of steam and carbon dioxide, the gas consists of 60% of hydrogen, 38% of the methane and 2% of carbon monoxide.

At higher temperatures the gas will be richer in hydrogen but also there will be somewhat more carbon monoxide. The actual composition will depend on the composition of gas admitted, and on the relative rates of the three reactions. At 700° the methane-steam reactions are both 70–80% complete. By using an excess of steam the reaction to form carbon dioxide is favored, and an excess of steam also tends to reverse the water-gas reaction (111), removing carbon monoxide. There is thus the possibility of obtaining a gas which is largely hydrogen. If carbon monoxide is desired as well, a decrease in the steam concentration will increase the concentration of this gas.

It is to be noted that patents have been granted for the operation of these reactions at still higher temperatures.[6] A comprehensive investigation of the field has recently been published by Neumann and Jacob.[7] The reactions were carried out in both directions between 300 and 1000". Equilibrium was reached only above 800°.

Summary

1. The reaction, $CH_4 + 2H_2O$ $C02 + 4H_2$, has been studied at 500° and atmospheric pressure. Equilibrium has been approached from both sides and the value of the constant found to be 0.037 (partial pressures being expressed in atmospheres) at 505°. This is in excellent agreement with the value calculated from Lewis and Randall's free energy equations, and thus supports in particular their equation for methane in the low temperature region.

2. It is pointed out that the reactions $CH_4 + H_2O \rightleftarrows CO + 3H_2$ and $CO_2 + H_2 \rightleftarrows CO + H_2O$ are also to be taken into account at higher temperatures. Equilibrium constants at 500, 600 and 700" are given for reference.

3. Attention is called to the methane–steam reactions as a source of hydrogen and of hydrogen-carbon monoxide mixtures.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, THE ROOSEVELT HOSPITAL]

RED COMPOUNDS OF BARBITURIC ACID, PICRIC ACID AND SODIUM, OR LEAD, HYDROXIDE

BY ISIDOR GREENWALD

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Dox[1] has called attention to the red color obtained upon mixing solutions of barbituric acid, picric acid and sodium hydroxide. He stated that the color was due to the formation of picramic acid, although his only evidence therefor was the fact that the reaction mixture, treated with sulfanilic acid, sodium nitrite and acid, yielded yellow needles which appeared to be identical with those obtained from picramic acid under the same conditions.

It seemed to the writer that the matter was capable of more direct determination. His interest arose from the circumstance that Greenwald

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[6] Badische Anilin und Soda-Fabrik, British patent 12,978 (1913).

[7] Neumann and Jacob, *Z. Elektrochem.*, 30,557 *(1924)*.

[1] Dox, *Z. physiol. Chew.*, **150**, 118 (1925).

and Gross[2] had found that there was no reduction of the picric acid in Jaffe's reaction for creatinine, which had also been previously ascribed to the formation of picramic acid.[3] The similarity of the color produced in the reactions of creatinine and of barbituric acid with picric acid and sodium hydroxide led to the belief that the nature of the reactions might be the same.

Just as is the case with creatinine, no color is developed when barbituric acid solutions are treated with 2,4-dinitrophenol, or with 2,6-dinitrophenol, and sodium hydroxide. With trinitro-m-cresol and alkali, barbituric acid gives a slowly developing orange color that is quite different from the instantaneous dark red color obtained with alkaline picrate solutions.

Solutions of barbituric acid were treated with about 1.25 equivalents of picric acid and a considerable excess of sodium hydroxide. After varying intervals, the mixtures were acidified with acetic acid and the picric acid content was determined by precipitation with *nitron*.[4] It was found that the loss in picric acid was very slow and, within the first fifteen minutes, quite negligible. The depth of color in the reaction mixtures, diluted to facilitate comparison, reached its maximum in about fifteen minutes, thereafter diminishing slowly.

When the proportions of barbituric acid and of picric acid were varied, it was found that increasing the concentration of either the barbituric acid or the picric acid increased the depth of color. Apparently, under the conditions originally employed, the reaction did not reach completion but proceeded to an equilibrium between the red compound and its constituents.

It was also found that the maximum color development, under the conditions employed, required more than five times the amount of alkali needed to form sodium picrate and disodium barbiturate.

When hydrochloric acid was added to a concentrated solution of barbituric acid, picric acid and sodium hydroxide, no such red compound as was obtained with similar mixtures containing creatinine,[2] instead of barbituric acid, was precipitated. The yellow precipitate seemed to consist of barbituric acid and picric acid. When, however, the alkaline reaction mixture was run into five volumes of 95% alcohol, a red, flocculent precipitate was obtained. This was filtered out, dissolved in water and reprecipitated. The material was filtered out, dried over sulfuric acid *in vacuo* and analyzed. It appeared to be a compound of 3 moles of barbituric acid, 2 of picric acid, 9 of sodium hydroxide and 1 or 2 moles of water. Whether prepared from mixtures containing one or two moles of barbituric acid for each mole of picric acid, the composition of the precipitate was the same. When, however, precipitation was made from more dilute

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[2] Greenwald and Gross, J. Biol. *Chem.*, 59,601 (1924).

[3] Chapman, *Analyst,* 34,475 (1909).

[4] Busch and Blume, *Z. angew. Chem.*, 21,354 (1908).

mixtures, and using more alcohol, the precipitate yielded more picric acid and contained more non-picric nitrogen and less sodium than did the preparations from the more concentrated solutions. Apparently, in the dilute solutions, more dissociation occurred and some sodium picrate and some sodium barbiturate were also precipitated.

When heated at 78°, at about 300 mm., there was no appreciable loss in weight. After drying at 100°, also at 300 mm., the loss from Preparation II was 3.1%, corresponding to about 2 moles of water. The material now yielded only 31% of picric acid, or 30% of the original weight, upon solution, acidification and precipitation with nitron. One-sixth of the picric acid had been destroyed.

That both the picric acid and the barbituric acid could be recovered from the unheated red compound was shown by suitable experiments.

When a solution of the red compound was treated with basic lead acetate solution, a brick-red precipitate was obtained. This was filtered out, washed and dried in a vacuum desiccator over sulfuric acid. Two different preparations gave slightly different results upon analysis, but in both instances the ratio of picric acid nitrogen to total nitrogen indicated that the material contained two moles of picric acid for each three moles of barbituric acid. The lead content was considerably greater than that calculated for a compound containing 9 moles of lead hydroxide. The analyses agreed best with the formula 3 barbituric acid, 2 picric acid, 11 lead hydroxide.

In another paper[5] it has been shown that the addition of alcohol to a concentrated mixture of creatinine, picric acid and sodium hydroxide yielded a red compound containing 2 moles of creatinine, 1 of picric acid, 3 of sodium hydroxide and 3 of water. It is interesting to note, in both the creatinine and the barbituric acid compounds, that the picric acid furnishes one-half of the total nitrogen and that the amount of sodium hydroxide, after allowing for that required to form sodium picrate (and monosodium barbiturate) is the equivalent of 2 moles of sodium hydroxide for each mole of picric acid. The lead barbiturate–picrate compound differs from the analogous creatinine compound in that there is no loss of nitrogen when it is treated with concentrated hydrochloric acid or 65% sulfuric acid and in that the full color value of the barbituric acid present may be obtained on treatment with more sodium picrate and sodium hydroxide

There are a number of other compounds that give similar red colors with alkaline picrate solutions. It is intended to investigate the nature of the compounds formed.

Experimental

Recovery of Picric Acid from Mixtures of Barbituric Acid, Picric Acid and Sodium Hydroxide.—To 2cc. portions of a 1% barbituric acid (anhydrous) there were added

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[5] Greenwald, J. *Biol. Chem.*, May, 1928.

5 cc. of an approximately 1% picric acid solution and 1 cc. of 10% sodium hydroxide. After varying intervals, the mixtures were acidified with acetic acid, diluted with 100 cc. of water, heated to boiling and the picric acid was precipitated with nitron. Two controls were used. One of these contained no barbituric acid; in the other, the barbituric acid was added after the acidification with acetic acid. The weights of the nitron picrate obtained and the amounts of picric acid they represent are shown in Table I.

TABLE I

RECOVERY OF PICRIC ACID FROM MIXTURES CONTAINING BARBITURIC ACID, PICRIC ACID AND SODIUM HYDROXIDE

	Nitron picrate, g.	Picric acid, g.
Control without barbituric acid	0.1149	0.0486
Control with barbituric acid	.1143	.0484
After standing for five minutes	.1138	.0482
After standing for ten minutes	.1129	.0478
After standing for fifteen minutes	.1121	.0475
After standing for twenty minutes	.1098	.0465
After standing for forty minutes	.1021	.0433

Rate of Color Development.—To 2cc. portions of the same 1% barbituric acid solution, there were added 5cc. portions of 1% picric acid solution. After varying intervals, 1 cc. of 10% sodium hydroxide was added. All of the mixtures were diluted to 100 cc. at the same time. That in which the reaction had proceeded for three minutes was taken as the standard and was set at 10 mm. in a Duboscq colorimeter. The readings obtained with the other solutions are shown in Table II.

TABLE II

RATE OF COLOR DEVELOPMENT

Mixture diluted after three minutes as standard at 10 mm.

Mixtures diluted after	5 min.	10 min.	15 min.	30 min.
Readings	7.65 mm.	7.00 mm.	6.70 mm.	7.30 mm.

Effect of Concentration of Sodium Hydroxide upon the Development of Color.—To 2cc. portions of the same 1% barbituric acid solution there were added 5 cc. of 1% picric acid and varying amounts of 10% sodium hydroxide. After fifteen minutes, the mixtures were diluted to 100 cc. and compared in the colorimeter, using that prepared with 1 cc. of sodium hydroxide as the standard and setting it at 10 mm. The readings obtained are shown in Table III.

TABLE III

EFFECT OF THE CONCENTRATION OF SODIUM HYDROXIDE UPON THE INTENSITY OF THE COLOR

Mixture with 1.0 cc. of 10% sodium hydroxide as standard, set at 10 mm.

Sodium hydroxide used, cc.	0.4	0.6	0.8	1.4	1.6
Readings, mm.	18.0	12.0	10.5	8.9	8.9

Effect of Varying the Proportions of Barbituric Acid and Picric Acid upon the Intensity of the Color.—Into each of a series of 100cc. volumetric flasks, there were measured 2 cc. of the same 1% barbituric acid solution and 5, 10 and 15 cc. of 1% picric acid solution. Into another flask, there were measured 4 cc. of the barbituric acid and 5 cc. of the picric acid. Water was added to make the total volume in each flask 17 cc. After adding 2 cc. of 10% sodium hydroxide, the mixtures were allowed to stand for fifteen minutes and were then diluted to 100 cc. That prepared with 2 cc. of barbituric acid and **5** cc. of picric acid was taken as the standard and was set at **10** mm. Table IV contains the readings obtained with the other mixtures.

TABLE IV

EFFECT OF VARYING THE PROPORTIONS OF BARBITURIC ACID AND PICRIC ACID UPON THE INTENSITY OF THE COLOR

Mixture containing **2** cc. of 1% barbituric acid and **5** cc. of 1% picric acid used as the standard and set at **10** mm.

Mixture	Readings, mm.
2 cc. of barbituric acid + **10** cc. of picric acid + **2** cc. of 10% sodium hydroxide	**7.00**
2 cc. of barbituric acid + **15** cc. of picric acid + **2** cc. of 10% sodium hydroxide	**6.40**
4 cc. of barbituric acid + 5 cc. of picric acid + **2** cc. of 10% sodium hydroxide	**6.40**

Preparation of the New Compound of Barbituric Acid, Picric Acid and Sodium Hydroxide.—(The details are those of Preparation VII.) To **8.69** g. of anhydrous barbituric acid, dissolved in **150** cc. of hot water, there was added **8** cc. of **6** N sodium hydroxide. To **15.36** g. of picric acid, dissolved in **300** cc. of hot water, there was added **5** cc. of **6** N sodium hydroxide; after mixing and cooling, 50 cc. of **6** N sodium hydroxide was added and the mixture was allowed to stand for ten minutes. It was then run into **3000** cc. of **95%** alcohol. The flocculent precipitate was filtered out, dissolved in about 400 cc. of water and reprecipitated by running into 3000 cc. of 95% alcohol. The precipitate thus obtained was filtered out and dried at about **20** mm. over sulfuric acid; yield **21.2** g.; calculated yield about **28** g.

Analysis of the New Sodium Compound—Weighed quantities were dissolved in water, the solution was acidified with acetic acid, and picric acid was then determined by precipitation with nitron. The filtrate from the nitron picrate was evaporated to 50 to **100** cc., about **1** cc. of nitric acid was added and the nitron nitrate was allowed to crystallize. After filtering this out, a few drops of concentrated sulfuric acid were added and the solution was evaporated in a platinum crucible. The residue was ignited and weighed. In a few instances the identity of the residue as sodium sulfate was established by conversion to barium sulfate and weighing as such. Total nitrogen was determined by the Kjeldahl method, after reduction with tin and hydrochloric acid. The same

TABLE V

ANALYSES OF THE NEW SODIUM AND LEAD COMPOUNDS CONTAINING PICRIC AND BARBITURIC ACIDS

Preparation	Total nitrogen	Picric acid	Sodium	Preparation	Total nitrogen	Picric acid	Sodium
I	13.6	37.2	17.1	Calcd. for compd. of 3 barbituric acid, 2 picric acid, 9 NaOH, 1 H_2O	13.78	37.55	16.97
II	13.5	36.5	16.6				
III	13.8	36.7	17.5				
IV (from dil. soln.)	(14.3)	(41.1)	(15.6)				
V (IV, redissolved and repptd. from concd. soln.)	13.8	38.1	17.4	Same, with 2 moles of H_2O	13.58	37.00	16.72
				Lead compound			**Lead**
VI	13.8	37.2	16.5	VIII (from III)	4.94	13.1	63.0
VII	13.7	37.3	17.1	IX (from VI)	4.62	12.8	65.1
				Calcd. for compd. of 3 barbituric acid, 2 picric acid, 11 lead hydroxide	4.81	13.1	65 2

values were obtained whether or not the material was first treated with dilute acetic acid.

Analysis of the New Lead Compound.—Two preparations of the lead compound were made by adding basic lead acetate solution to solutions of Preparations III and VI, respectively. The precipitates were filtered out, washed and dried in a vacuum desiccator. Picric acid was determined by dissolving weighed portions in dilute acetic acid and precipitating with nitron. Total nitrogen was determined by the Kjeldahl method, after reduction with tin and hydrochloric acid. The same values were obtained when the substance was treated directly with hot 65% sulfuric acid or with concentrated hydrochloric acid as when it was first dissolved in dilute acetic acid. Lead was determined by decomposition with sulfuric acid and also by precipitation as the sulfide from the filtrate from the nitron picrate, with subsequent oxidation to the sulfate. The amounts of lead sulfate obtained by the two methods were identical.

Isolation of Picric and Barbituric Acids from the New Substance.—Six grams of Preparation VII were dissolved in 200 cc. of water. After adding 10 cc. of concentrated hydrochloric acid, the solution was extracted with benzene in a continuous extraction apparatus, keeping the acid liquid cooled. The benzene was evaporated and the residue was dried at 110°. It weighed 2.24 g., or 37.3% of the amount of material taken. It required 91.0 cc. of 0.1073 N sodium hydroxide for neutralization. This is the exact equivalent of 2.24 g. of picric acid. The extracted liquid was evaporated, in *vacuo*, to about. 60 cc. The crystals that separated were filtered out and recrystallized from water. They melted at 245°, the melting point of pure barbituric acid, and the melting point of a mixture of the two was also 245°. The nitrogen content was 17.1% and the loss in weight at 110° was 22.0%, which figures are those of the calculated nitrogen and water content of barbituric acid. The yield was 1.64 g., without correction for the solubility of barbituric acid in the 100 cc. of mother liquid. The calculated yield is 2.42 g.

The solubility of barbituric acid in water at the temperatures employed is about 1%. It is probably somewhat less in the presence of hydrochloric acid but it is not possible that the correction for solubility in the 60 cc. of acid liquid and in the 40 cc. of water employed for the recrystallization can be much less than the difference, 0.78 g., between the calculated and the observed yields.

Summary

By the addition of alcohol to a mixture of solutions of barbituric acid, picric acid and sodium hydroxide, a red precipitate is obtained. This, upon analysis, was found to contain 3 moles of barbituric acid, 2 of picric acid, 9 of sodium hydroxide and 1 or 2 moles of water. The addition of basic lead acetate to a solution of the new sodium compound yields a red precipitate which contains 3 moles of barbituric acid, 2 of picric acid and 11 of lead hydroxide.

NEW YORK CITY

[Contribution from the Department of Chemistry, University of Illinois]

CYCLOHEXYL AND CYCLOHEXYLMETHYL ALKYL ACETIC ACIDS AND THEIR ACTION TOWARD B. LEPRAE. X[1]

By Roger Adams, W. M. Stanley, and H. A. Stearns[2]

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In a previous paper, the preparation of three series of acids was described, β-cyclohexylethyl, γ-cyclohexylpropyl and δ-cyclohexylbutyl alkyl acetic acids. Of these acids those containing from 16 to 18 carbon atoms were found to have an especially high bactericidal action toward B. *Leprae* and a distinctly greater effect than the isomeric acids with the carboxyl group at the end of the side chain.

In this investigation the two series, cyclohexyl (I) and cyclohexylmethyl (II) alkyl acetic acids were made and tested, where the R in (I)

$$\underset{\text{I}}{C_6H_{11}CH(CO_2H)R} \qquad \underset{\text{II}}{C_6H_{11}CH_2CH(CO_2H)R}$$

represents alkyl groups varying in size from ethyl to lauryl and the R in (II) from ethyl to n-octyl. In these series, also, the most effective acids were those containing 16 to 18 carbon atoms, as may be seen in Table I.

TABLE I

BACTERIOLOGICAL TESTS TO B. *Leprae*

	Dilutions of sodium salts in thousand																								
	10	20	30	40	50	60	70	80	90	100	110	120	110	140	150	160	170	180	190	200	220	240	260	280	300	320	340
Cyclohexyl alkyl acetic acids, $C_6H_{11}CH(CO_2H)R$. R =																										
n-C_5H_{11}	−	−	+	+	+	+	+	+	+	+					+					+							
n-C_6H_{13}	−	−	−	−	±	+	+	+	+	+					+					+							
n-C_7H_{15}	−	−	−	−	−	−	−	−	−	−	±	+	+	±	+	+	+	+	+	+			+		+		
n-C_8H_{17}	−	−	−	−	−	−	−	−	−	−	−	+	+	±	±	−	+	+	+	+			+		+		
n-C_9H_{19}	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	+	−	±	+	−	+		
n-$C_{10}H_{21}$										−	−	−	−	−	−	−	−	−	±	±			+		+		
n-$C_{11}H_{23}$										−	−	−	−	−	−	−	±	−	−	±			+		+		
n-$C_{12}H_{25}$	−	−	−	−	−	−	±	±	±	±	±	±	+	+	+	±	+	−	+								
Cyclohexylmethyl alkyl acetic acids, $C_6H_{11}CH_2CH(CO_2H)R$. R =																										
C_2H_5	−	−	+	+	+	+	+	+	+	+																	
n-C_3H_7	+	+	+	+	+	+	+	+	+	+																	
n-C_4H_9	−	+	+	+	+	+	+ -	| -	+	+																	
n-C_5H_{11}	−	−	−	−	−	±	+	+	+	+																	
n-C_6H_{13}	−	−	−	±	+	±	±	±	+	+																	
n-C_7H_{15}	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	±	+	+	+	±	−	±	±
n-C_8H_{17}	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	±	−	±	+	−	−	±	±

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[1] Previous papers in this field are: (a) Shriner and Adams, This Journal, 47, 2727 (1925); (b) Noller with Adams, *ibid.*, 48, 1074 (1926); (c) 48, 1080 (1926); (d) Hiers with Adams, *ibid.*, 48, 1089 (1926); (e) Van Dyke and Adams, *ibid.*, 48, 2393 (1926); (f) Sacks with Adams, *ibid.*, 48, 2395 (1926); (g) Hiers with Adams, *ibid.*, 48, 2385 (1926); (h) Adams, Stanley, Ford and Peterson, *ibid.*, 49, 2934 (1927); (i) Arvin and Adams, *ibid.*, 49, 2940 (1927).

[2] This communication is an abstract of portions of theses presented by W. M. Stanley and H. A. Stearns in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, in Chemistry, at the University of Illinois.

As in the first three series studied a certain molecular weight appears to be necessary before bactericidal action is found and it then increases with molecular weight until a maximum figure is reached.

In order to have a direct comparison of isomeric acids in these cyclohexyl series, where the carboxyl is on the first, second, third, fourth and fifth carbon atoms, respectively, from the ring, Table II has been arranged selecting, however, merely the most bactericidal acids.[1h] The dilutions of the sodium salts, which represent the maximum values that will kill with certainty, are listed for each isomer.

TABLE II

COMPARISON OF BACTERICIDAL VALUE OF CERTAIN ISOMERS OF FIVE CYCLOHEXYL SERIES

	R =	Maximum dilution of sodium salts in thousands
$C_6H_{11}CH(CO_2H)R$	C_8H_{17}	110
	C_9H_{19}	190
	$C_{10}H_{21}$	180
$C_6H_{11}CH_2CH(CO_2H)R$	C_7H_{15}	190
	C_8H_{17}	190
	C_9H_{19}	. . .
$C_6H_{11}(CH_2)_2CH(CO_2H)R$	C_6H_{13}	160
	C_7H_{15}	220
	C_8H_{17}	320
$C_6H_{11}(CH_2)_3CH(CO_2H)R$	C_5H_{11}	170
	C_6H_{15}	240
	C_7H_{15}	220
$C_6H_{11}(CH_2)_4CH(CO_2H)R$	C_4H_9	190
	C_5H_{11}	220
	C_6H_{13}	180

It is obvious that the location of the carboxyl group on the chain has comparatively little effect. Although the acids of the cyclohexylethyl and cyclohexylpropyl series appear to kill in somewhat higher dilutions than the isomers in the other series, it may be stated that the errors in bacteriological work are large, and much more evidence should be available before there would be safety in such a conclusion.

The acids of Series I were prepared by condensing the proper alkyl halides with cyclohexyl malonic ester and saponifying. The acids of Series II were made also by saponification of the corresponding malonic esters. Cyclohexylmagnesium bromide and formaldehyde gave cyclohexylcarbinol, which in turn was converted to the bromide[1g] and condensed with malonic ester. The alkyl groups of varying sizes were then introduced.

Experimental

Alkyl Halides.—Most of these were prepared as described in a previous paper.[1h] Those used in this investigation which have not been employed before were n-decyl bromide, n-undecyl bromide and lauryl bromide. They were all made from the corresponding alcohols with hydrobromic acid and sulfuric acid, and all but the first will be described in more detail in the following paper.

Substituted Malonic Esters.—These were prepared as previously described. Cyclohexyl malonic ester and cyclohexylmethyl malonic ester were condensed with alkyl bromides. Part of the condensations were carried out as in the earlier investigations and part in an inert solvent. The latter seemed to give better yields.

Substituted Malonic Acids.—A slight modification of the procedure used previously proved advantageous. The disubstituted malonic esters were shaken with an excess of hot, saturated alcoholic potassium hydroxide solution and then refluxed overnight. The condenser was removed and the alcohol allowed to evaporate. The last traces of alcohol were then removed by heating under diminished pressure for two or three hours to 120° in an oil-bath. The solid potassium salt was dissolved in a little water and a small amount of ether added, the latter to take care of any unsaponified ester. The mixture was poured into a separatory funnel and the aqueous solution of potassium salt drawn off and run into an excess of ice and hydrochloric acid. During this neutralization the mixture should be shaken or stirred well and also for several minutes afterwards. The free malonic acid was extracted with ether. This may be purified from benzene or acetone, or in a crude state converted directly

TABLE III

DIETHYL CYCLOHEXYL ALKYL MALONATES. $C_6H_{11}C(CO_2C_2H_5)_2R$

R =	B. p., °C. (2 mm.)	n^{25}_D	d^{25}_4	Calcd., % C	Calcd., % H	Found, % C	Found, % H
n-C_5H_{11}	121–125	1.4553	0.9850	69.17	10.33	69.31	10.26
n-C_6H_{13}	126–130	1.4559	.9755	69.88	10.50	70.28	10.65
n-C_7H_{15}	135–139	1.4562	.9685	70.52	10.66	70.41	10.75
n-C_8H_{17}	144–148	1.4564	.9638	71.12	10.81	71.45	10.79
n-C_9H_{19}	149–154	1.4567	.9574	71.67	10.94	71.66	10.85
n-$C_{10}H_{21}$	157–161	1.4570	.9540	72.19	11.07	72.58	10.87
n-$C_{11}H_{23}$	170–175	1.4574	.9532	72.66	11.18	72.31	11.12
n-$C_{12}H_{25}$	185–189	1.4589	.9466	73.14	11.29	72.63	11.22

TABLE IV

DIETHYL CYCLOHEXYLMETHYL ALKYL MALONATES. $C_6H_{11}CH_2C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n^{20}_D	d^{20}_4	Calcd., % C	Calcd., % H	Found, % C	Found, % H
C_2H_5	143–145 (4.5 mm.)	1.4542	1.0104	67.55	9.92	67.75	10.02
n-C_3H_7	154–155 (3 mm.)	1.4529	1.0062	68.41	10.13	67.69	10.11
n-C_4H_9	157–159 (4.5 mm.)	1.4548	0.9910	69.18	10.33	69.07	10.19
n-C_5H_{11}	159–160 (4 mm.)	1.4558	.9853	69.89	10.50	69.57	10.52
n-C_6H_{13}	160–163 (2.5 mm.)	1.4544	.9721	70.53	10.66	70.66	10.89
n-C_7H_{15}	183–185 (5 mm.)	1.4560	.9679	71.13	10.88	71.76	11.02
n-C_8H_{17}	178–181 (3 mm.)	1.4570	.9612	71.68	10.94	71.28	10.91

to the monobasic acid. Since many of the malonic acids had properties which rendered them difficult to purify completely, most of them were converted directly to the monobasic acids.

Monobasic Acids.—These acids were prepared by heating the malonic acid for several hours under reflux to 20–30° above their melting points.

TABLE V

CYCLOHEXYLMETHYL ALKYL MALONIC ACIDS. $C_6H_{11}CH_2C(CO_2H)_2R$

R =	M. p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
C_2H_5	127.5–130	63.12	8.83	62.94	8.91
n-C_3H_7	145–147	64.71	9.15	64.76	9.03
n-C_4H_9	132–134	65.59	9.44	65.95	9.49
n-C_5H_{11}	132–135	66.62	9.70	66.37	9.56

TABLE VI

CYCLOHEXYL ALKYL ACETIC ACIDS. $C_6H_{11}CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
n-C_5H_{11}	136–139 (3 mm.)	1.4640	0.9544	73.51	11.40	73.31	11.25
n-C_6H_{13}	145–149 (3 mm.)	1.4641	.9449	74.27	11.58	74.44	11.45
n-C_7H_{15}	148–152 (2 mm.)	1.4641	.9350	74.92	11.75	74.74	11.66
n-C_8H_{17}	158–161 (2 mm.)	1.4642	.9298	75.52	11.89	75.88	11.97
n-C_9H_{19}	167–171 (3 mm.)	1.4645	.9245	76.04	12.02	75.56	11.66
n-$C_{10}H_{21}$	165–169 (2 mm.)	1.4649	.9224	76.51	12.14	76.98	11.91
n-$C_{11}H_{23}$	173–177 (2 mm.)	1.4650	.9166	76.95	12.25	76.72	12.01
n-$C_{12}H_{25}$	187–191 (2 mm.)	1.4653	.9129	77.34	12.34	76.91	12.27

TABLE VII

CYCLOHEXYLMETHYL ALKYL ACETIC ACIDS. $C_6H_{11}CH_2CH(CO_2H)R$

R =	B. p., °C.	n_D^{25}	d_4^{25}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
C_2H_5	131–132 (2 mm.)	1.4623	0.9814	71.68	10.94	71.34	10.96
n-C_3H_7	141–143 (4.5 mm.)	1.4628	.9720	72.66	11.18	72.10	10.93
n-C_4H_9	133–136 (3 mm.)	1.4620	.9564	73.52	11.40	73.74	11.45
n-C_5H_{11}	139–142 (2 mm.)	1.4630	.9516	74.27	11.58	73.83	11.53
n-C_6H_{13}	174–175 (3 mm.)	1.4627	.9448	74.94	11.74	74.82	11.91
n-C_7H_{15}	202–204 (3 mm.)	1.4632	.9393	75.52	11.89	75.28	11.81
n-C_8H_{17}	186–190 (4 mm.)	1.4640	.9331	76.05	12.02	75.77	11.94

Summary

Two series of acids, cyclohexyl alkyl acetic acids and cyclohexylmethyl alkyl acetic acids have been prepared and their bactericidal effect toward B. *Leprae* determined. Those acids having 16 to 18 carbon atoms were especially effective.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A NEW METHOD FOR THE PREPARATION OF O,N-DIALKYLHYDROXYLAMINES

BY RANDOLPH T. MAJOR AND ELMER E. FLECK

RECEIVED MARCH 5, 1928 PUBLISHED MAY 5, 1928

The present methods used in the preparation of O,N-dialkylhydroxylamines[1] were found to be inadequate and too expensive to produce the relatively large amounts of these compounds required in the recent work in this Laboratory.

Hydroxyurethan prepared by Jones' modification of Hantzsch's method[2] was alkylated with a little more than two moles of dialkyl sulfate in alkaline solution. A small amount of O-alkylhydroxyurethan was separated by extraction with alkali from the O,N-dialkylhydroxyurethan which was formed during the reaction. These O,N-dialkylhydroxyurethans were hydrolyzed by refluxing them with a 50% solution of potassium hydroxide in alcohol. The free O,N-dialkylhydroxylamine was distilled into hydrochloric acid and recovered in the usual manner. O,N-dimethyl- and O,N-diethylhydroxylamines were prepared by this method.

A study of the boiling points of mixtures of O,N-dialkylhydroxylamines with water revealed a constant boiling mixture of O,N-diethylhydroxylamine and water at 74°. No corresponding mixture could be detected in the case of O,N-dimethylhydroxylamine and water.

Experimental Part

Preparation of O,N-Dimethylhydroxyurethan, $CH_3ONCH_3COOC_2H_5$.—Two moles of hydroxyurethan was dissolved in **1200** cc. of a **20%** solution of potassium hydroxide and to this was added, in small portions, with vigorous shaking, **4.25** moles of dimethyl sulfate. During this operation the temperature was kept below 25°. An oily layer soon appeared above the aqueous solution. The mixture was stirred vigorously for one hour after the addition of the dimethyl sulfate had been completed. The mixture was then made acid to congo red with sulfuric acid and extracted with ether; the ether solution was then extracted with **400** cc. of a **20%** solution of sodium hydroxide in 100cc. portions. The ether layer was dried with anhydrous sodium sulfate, the ether removed by distillation and the oil which remained distilled in *vacuo*. The portion boiling below 80° under **25** mm. was collected. O,N-dimethylhydroxyurethan was then separated by fractionation at atmospheric pressure. The portion boiling between **150** and 155°[3] was collected; yield, **80** g. The fraction which was left, after the O,N-dimethylhydroxyurethan had been distilled, decomposed when an attempt was made to distil it. A copious quantity of formaldehyde was present among the products of decomposition.

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[1] (a) Lossen, **Ann.**, 252, **230 (1889);** (b) Jones, *Am. Chem.* **J., 20, 40 (1898);** (c) **38, 253 (1907);** (d) Hecker, **ibid., 50, 444 (1913);** (e) Jones and Neuffer, THIS JOURNAL, **36,2202 (1914)**; (f) Neuffer and Hoffman, *ibid.*, **47,1685** (1925).

[2] Hantzsch, *Ber.*, 27, **1254 (1894);** ref. **lb**, p. **39.**

[3] Jones, ref. **lb**, p. **42,** gives 150–155° as the b. p.

The sodium hydroxide extract, from the above procedure, was made acid to congo red, extracted with ether and the ether solution dried with calcium chloride. Eleven g. of O-methylhydroxyurethan was obtained; b. p. 186–188°.[4]

Preparation **of O,N-Diethylhydroxyurethan, $C_2H_5ONC_2H_5COOC_2H_5$.**—To a solution of 2 moles of hydroxyurethan and 4.25 moles of diethyl sulfate was added, in small portions accompanied by vigorous shaking, 1200 cc. of a 20% solution of potassium hydroxide. Heat rapidly developed in the mixture. The temperature was allowed to rise to 65° and was maintained between 60 and 65° throughout the course of the reaction. More alkali was not added in any case until the rise in temperature produced by the previous addition had ceased. An oily layer appeared above the aqueous solution. After all of the potassium hydroxide had been added the mixture was vigorously stirred for an hour, cooled, made acid to congo red with sulfuric acid and extracted with ether. This ether solution was then extracted with 400 cc. of a 20% solution of sodium hydroxide in 100cc. portions. The ether solution was dried with anhydrous sodium sulfate, the ether distilled and the resulting oil fractionated *in vacuo*. The fraction boiling between 107 and 112° under 70 mm.[5] was recovered; yield, 162 g.

The sodium hydroxide extract from the above procedure was made acid to congo red, extracted with ether and the ether solution dried with calcium chloride. Eighteen g. of O-ethylhydroxyurethan was recovered; b. p. 195–196°.[6]

Preparation **of O,N-Dialkylhydroxylamines, RONRH.**—One mole of O,N-dialkylhydroxyurethan was added to a cold solution of 3 moles of potassium hydroxide dissolved in 350 cc. of 50% alcohol. Hydrolysis, accompanied by considerable heat, at once commenced. The solution was refluxed for one hour. The O,N-dialkylhydroxylamine was then distilled into ice-cooled dilute hydrochloric acid. The hydrochloric acid solution was concentrated on the water-bath and then placed in a vacuum desiccator containing concentrated sulfuric acid and solid potassium hydroxide. O,N-dimethylhydroxylammonium chloride separated in the form of white crystals. It was recrystallized from absolute alcohol by addition of dry ether; m. p. 115–116°. The O,N-diethylhydroxylammonium chloride remained as an oil.

To prepare O,N-dialkylhydroxylamine the hydrochloride was distilled with an excess of concentrated potassium hydroxide solution and the vapors passed over solid pieces of potassium hydroxide heated to 95° before they were condensed. O,N-dimethylhydroxylamine distilled at 4243° and corresponded in every respect to this compound as described by Jones.[7] O,N-diethylhydroxylamine distilled at 83° and had the same properties as those ascribed to it by Lossen.[8]

The Effect of Water upon the Boiling Point of O,N-Diethylhydroxylamine.—A solution of molecular equivalents of O,N-diethylhydroxylamine and water distilled at 74°. When a second molecular equivalent of water was added, two layers appeared. The upper layer distilled at 74° and then the temperature of the vapors rapidly rose to that of boiling water. The fraction distilling at 74° was dried over solid potassium hydroxide and redistilled; b. p. 83°.

The authors wish to express their appreciation to Professor Lauder W. Jones for many helpful suggestions and criticisms.

[4] Jones, ref. 1b, p. 41, gives 186–188° as the b. p.

[5] Hecker, ref. 1d, p. 449, gives 107–112° (70 mm.) as the b. p.

[6] Jones, ref. 1b, p. 45, gives 195–196° as the b. p.

[7] Jones, ref. 1b, p. 44, gives 42.2–42.6° as the b. p.

[8] Lossen, ref. 1a, p. 234, gives 83° as the b. p.

Summary

1. O,N-dialkylhydroxyurethans have been prepared by the action of alkyl sulfates on hydroxyurethan.

2. O,N-dialkylhydroxylamines have been obtained by hydrolysis of O,N-dialkylhydroxyurethans with alcoholic potassium hydroxide.

3. The addition of water has been shown to lower the boiling point of O,N-diethylhydroxylamine but not that of O,N-dimethylhydroxylamine.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

5-BROMO-2,4-DIMETHOXYBENZOYLACRYLIC ACID AND ITS ESTERS. II

BY GRACE POTTER RICE

RECEIVED MARCH 13, 1928 PUBLISHED MAY 5, 1928

In a study[1] of bromodimethoxybenzoylacrylic acid it has been found that the esters of this unsaturated y-ketonic acid readily form addition products with alcohols in the presence of a trace of potassium hydroxide. This reaction suggested an investigation of the behavior of the dibromo addition products of the acid and its esters on treatment with alkaline reagents under conditions which would favor the formation of acetylenic compounds as intermediate products.

On treatment with bromine, bromodimethoxybenzoylacrylic acid gives one dibromo acid, but under the same conditions the methyl and ethyl esters give mixtures of racemic compounds which were separated only after tedious fractional crystallization; the pairs of isomers have practically the same solubilities in the common organic solvents and the two racemic methyl esters have melting points within one degree of each other.[2] The mixture of racemic dibromomethyl esters was shown to give the same products with sodium methylate as the higher melting one of the isomers; in subsequent work therefore the mixtures of both dibromo esters were used.

The products obtained are alkoxy and hydroxy compounds which can be explained as addition products of bromodimethoxybenzoylpropiolic ester, formed by loss of two molecules of hydrogen bromide from the dibromo esters. No attempt has been made to isolate the acetylenic compounds, which would be expected to show the same ease of addition as the corresponding ethylenic esters.[1] Pairs of ethylenic bromo isomers, however, have been prepared from the dibromo methyl and ethyl esters and one of these ethylenic bromo methyl esters has been shown to give the same products as the saturated dibromo ester on treatment with a methyl alcohol solution of potash. That a second molecule of hydrogen bromide

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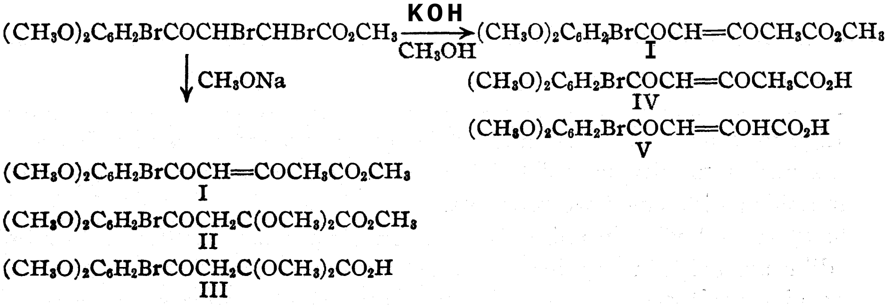
[1] Rice, THIS JOURNAL, 50,229 (1928).

[2] Lutz, *ibid.*, 48,2905 (1926).

is eliminated from the ethylenic bromo ester and that addition takes place to the resulting acetylenic compound seems beyond doubt from the recent work of Lutz[2] on 1,4-diketones. He has shown that dibenzoylacetylene is an intermediate product in the reaction of sodium acetate on dibenzoyldibromo-ethane and that it gives the same products of reaction as the dibromo compound.

The dibromo methyl ester of bromodimethoxybenzoylpropionic acid, on treatment with a concentrated solution of potassium hydroxide in methyl alcohol, gives as the chief product of reaction an unsaturated methoxy ester, I; there are also formed small quantities of the corresponding unsaturated methoxy acid, IV, an unsaturated hydroxy acid, V, and a considerable amount of material which was not identified.

With sodium methylate, however, the reaction is rapid and can be controlled so that any one of three substances, I, II, III, may be the chief product; a small quantity of the hydroxy acid, V, is formed in every reaction.



$$(CH_3O)_2C_6H_2BrCOCHBrCHBrCO_2CH_3 \xrightarrow[CH_3OH]{KOH} \underset{\text{I}}{(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2CH_3}$$

$$\underset{\text{IV}}{(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2H}$$

$$\underset{\text{V}}{(CH_3O)_2C_6H_2BrCOCH{=}COHCO_2H}$$

$$\downarrow CH_3ONa$$

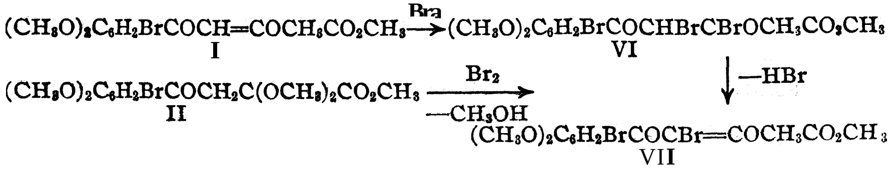
$$\underset{\text{I}}{(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2CH_3}$$

$$\underset{\text{II}}{(CH_3O)_2C_6H_2BrCOCH_2C(OCH_3)_2CO_2CH_3}$$

$$\underset{\text{III}}{(CH_3O)_2C_6H_2BrCOCH_2C(OCH_3)_2CO_2H}$$

That the substituents in these substances are in the alpha position is indicated by the fact that the esters of bromodimethoxybenzoylacrylic acid form addition products when treated with alcohols, in the presence of potassium hydroxide, in which the alkoxyl groups have been proved to be in the alpha position.[1]

All of these substances are colorless except the acid, V, which is brilliant yellow. The methoxy ester, I, and the hydroxy acid, V, decolorize a cold solution of potassium permanganate and add bromine quantitatively in ice-cold solution. The methoxy ester, I, forms a dibromo addition product which loses hydrogen bromide on recrystallization, giving an unsaturated bromomethoxy ester; this same ester results from the bromination of the saturated dimethoxy ester, II. The bromine atom in the unsaturated substance is therefore in the beta position.



$$\underset{\text{I}}{(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2CH_3} \xrightarrow{Br_2} \underset{\text{VI}}{(CH_3O)_2C_6H_2BrCOCHBrCBrOCH_3CO_2CH_3}$$

$$\underset{\text{II}}{(CH_3O)_2C_6H_2BrCOCH_2C(OCH_3)_2CO_2CH_3} \xrightarrow[-CH_3OH]{Br_2}$$

$$\downarrow -HBr$$

$$\underset{\text{VII}}{(CH_3O)_2C_6H_2BrCOCBr{=}COCH_3CO_2CH_3}$$

The unsaturated hydroxy acid, V, adds the calculated amount of bromine at 0° but hydrogen bromide is eliminated slowly and the product which separates in quantitative yield is probably the diketone, $(CH_3O)_2C_6H_2BrCOCHBrCOCO_2H$. That the acid, V, has not the keto form $(CH_3O)_2C_6H_2BrCOCH_2COCO_2H$ but the enol form as written or enolizes with extreme rapidity at 0° was established by the Kurt Meyer titration method. It reacts in absolute ether solution with one molecular equivalent of diazomethane to give a brilliant yellow ester; this forms a copper derivative and is an enol as shown by the Kurt Meyer titration method. The enolic ester reacts with a second molecular equivalent of diazomethane to give a colorless methoxy ester (113°) which is the geometrical isomer of the methoxy ester, I, since it gives the same dibromo compound as this substance on treatment with bromine.

The quantitative transformation of the acid, III, into the ester, II, indicates the relationship between these substances. That their two methoxyl groups are attached to the same carbon atom[3] is indicated by the behavior of the substances with acids. The dimethoxy ester, II, is transformed by cold, concd. hydrochloric acid into a bright yellow ester identical with that formed from the hydroxy acid, V, on treatment with diazomethane. This same yellow ester is obtained on treatment of the unsaturated methoxy ester, I, with concd. hydrochloric acid. The dimethoxy acid, III, loses its methoxyl groups much more readily than its ester, for it is changed completely into the unsaturated hydroxy acid, V, even on recrystallization from glacial acetic acid.

The unsaturated methoxy acid, IV, is the only one of the five products from the reactions with the dibromo ester which cannot be obtained in any quantity desired; only traces of it were separated in the reactions with the dibromo ester but a small amount of it was formed when the dibromo acid was treated with a concd. solution of potassium hydroxide in methyl alcohol. Treatment of the dibromo acid with a concd. solution of potassium hydroxide in ethyl alcohol gave the corresponding unsaturated ethoxy acid; this reaction proves the structure of the substance, IV.

The relationships of the substances are shown in the following scheme.

The dibromo ethyl ester gives with the alkaline reagents used products analogous to all those obtained from the dibromo methyl ester with one interesting exception; the diethoxy acid corresponding to the acid, III, is not formed. The dibromo acid, on the other hand, is remarkably unreactive compared with its esters; with sodium methylate only one molecule of hydrogen bromide is eliminated and the products of reaction are unsaturated bromo acids.

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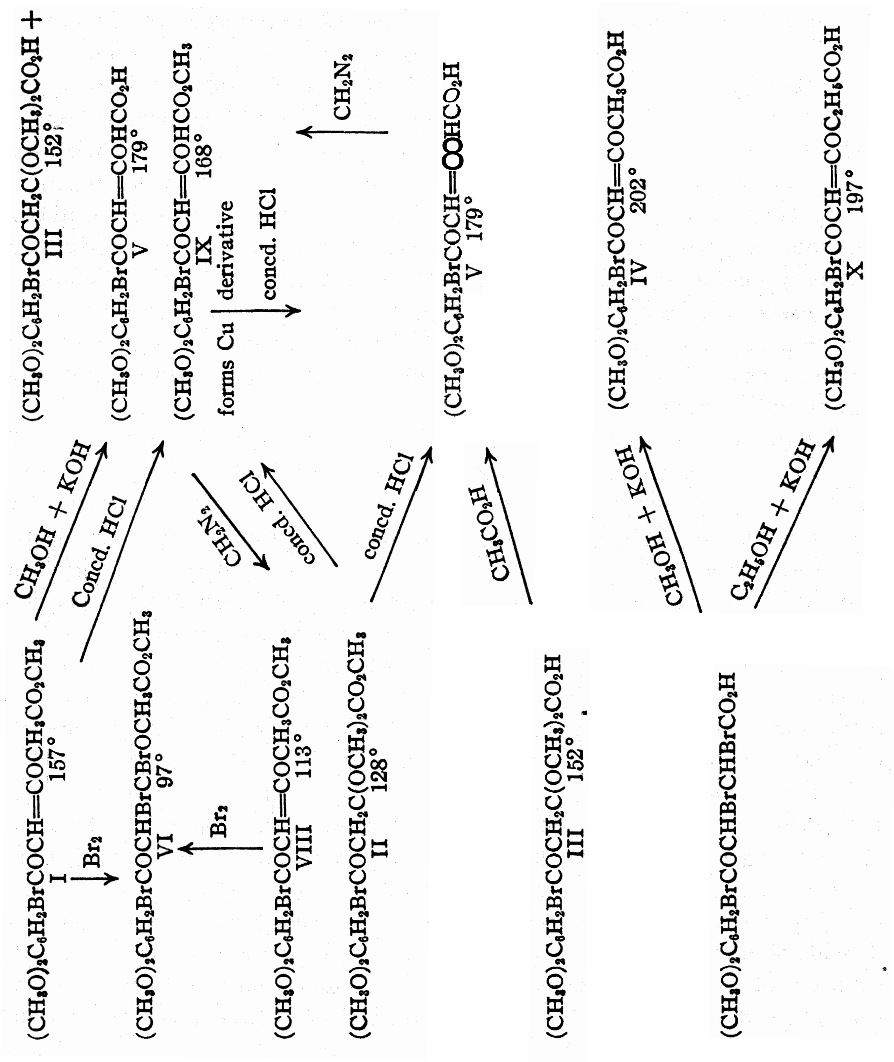
[3] Michael and Bucher, *Ber.*, 29, 1792 (1896); Moureu, *Compt. rend.*, 137, 269 (1903).



Experimental Part

Methyl **α,β-Dibromo-5-bromo-2,4-dimethoxybenzoylpropionate,** $(CH_3O)_2C_6H_2Br$-$COCHBrCHBrCO_2CH_3$.—The reaction between methyl 5-bromo-2,4-dimethoxybenzoylacrylate and bromine was carried out in the usual way with chloroform as a solvent; the crude product was obtained in quantitative yield. It is a mixture of isomers from which the higher melting one can be separated by warming the mixture with methyl alcohol and recrystallizing the undissolved portion from the same solvent; a 70–80% yield of ester melting at 150.5° was thus obtained. The filtrates contain a mixture from which a small quantity of a second isomer (149–150°) was isolated by tedious picking apart of two kinds of crystals and fractional recrystallization from methyl alcohol. It was not found possible to separate the rest of the product, which invariably crystallized from all the solvents used in mixed crystals which began to melt at about 127"; the mixture of the two pure isomers had this same melting point.

Anal. Calcd. for $C_{13}H_{13}O_5Br_3$: C, 31.91; H, 2.65. Found: I (150.5") C, 32.12; H, 2.72. II (149–150°) C, 32.39; H, 2.66.

After it was found that the mixture of isomers gave the same products as the isomer (150.5') with alkaline reagents, the crude product was washed with boiling methyl alcohol and used in subsequent reactions.

Methyl Bromo-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH{=}CBrCO_2CH_3$ or $(CH_3O)_2C_6H_2BrCOCBr{=}CHCO_2CH_3$.—Two unsaturated bromo esters were formed when the mixture of dibromo esters was heated for thirty minutes in methyl alcohol solution with potassium acetate. The solid which was precipitated by adding ice to the solution was dried—yield 80%—and dissolved in methyl alcohol; a solid crystallized in fine, lemon-colored needles melting at 139° and after partial evaporation of the filtrate a colorless solid separated in heavy, transparent crystals melting at 164°; after one such treatment about 30% of the crude product was left as a mixture of the two substances. The yellow needles are very sensitive to light and are transformed slowly in diffused daylight and very rapidly in the sunlight into the colorless solid. The mixture of isomers was exposed to the sunlight until it had lost its yellow color; the colorless solid then melted at 164°. This isomerization in the light proves that the two substances are geometrical and not structural isomers.

Anal. Calcd. for $C_{13}H_{12}O_5Br_2$: C, 38.23; H, 2.94. Found: I (139") C, 38.38; H, 2.79. II (164") C, 38.56; H, 2.87.

It has not been found possible up to this time to determine whether the bromine atom in the side chain of these esters and related compounds is in the alpha or beta position; work with this aim in view is now in progress.

Reaction between the Dibromo Methyl Ester and Sodium Methylate

Methyl α-Methoxy-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2CH_3$, I.—This ester is obtained in 60% yield when the dibromo ester (4 g. in 70 cc. of methyl alcohol) is heated for thirty minutes on a boiling water-bath with the sodium methylate made by treating 10 cc. of methyl alcohol with 0.4 g. of sodium. The fine, white needles which separate as the solution cools are recrystallized from methyl alcohol; they melt at 157° and are not readily soluble in the common organic solvents.

Anal. Calcd. for $C_{14}H_{15}O_6Br$: C, 46.79; H, 4.17. Found: C, 46.81; H, 4.20.

The filtrate contains a mixture of substances which were not separated since further heating with sodium methylate transforms it into an acid, the same substance which is formed by heating the dibromo ester for an hour with two molecular equivalents of sodium methylate. The ester decolorizes a cold acetone solution of potassium permanganate but it is not reduced by sodium hydrosulfite. The lack of reactivity with this reducing agent was unexpected in view of the ease with which bromodimethoxybenzoylacrylie acid and its esters are reduced with sodium hydrosulfite. If its behavior on reduction had been like that of the ester of the unsaturated acid the product would have been α-methoxy-5-bromo-2,4-dimethoxybenzoylpropionate[1] and the position of the methoxyl group would have been established experimentally.

The ester reacts with bromine in chloroform solution at 0° to give a dibromo ester; the crude product solidified in contact with methyl alcohol and was purified by washing thrice with the ice-cold solvent. The yield of white powder was 90%.

Anal. Calcd. for $C_{14}H_{15}O_6Br_3$: C, 32.37; H, 2.89. Found: C, 32.45; H, 2.80.

The substance is not stable but changes on standing into a high melting solid which was not investigated; on recrystallization from methyl alcohol it loses hydrogen bromide and forms an unsaturated bromomethoxy ester which separates in clusters of fine needles melting at 123°. The bromine atom in this substance is in the alpha position, its formula, $(CH_3O)_2C_6H_2BrCOCBr=COCH_3CO_2CH_3$, being established by a second method of preparation. (See p. 1487,)

Anal. Calcd. for $C_{14}H_{14}O_6Br_2$: C, 38.35; H, 3.19. Found: C, 38.72; H, 3.68.

This unsaturated bromo ester is also formed if the chloroform solution is allowed to grow warm during the bromination of the unsaturated ester.

Methyl α-Hydroxy-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH=COHCO_2CH_3$.—The unsaturated methoxy ester is not changed by boiling for two hours in glacial acetic acid solution but it is hydrolyzed by stirring for ten minutes with concd. hydrochloric acid. Ice was added to the solution, the precipitated solid filtered off and recrystallized from methyl alcohol; it separates in brilliant yellow needles melting at 168°. The ester forms an olive green copper compound when treated in ether solution with copper acetate and gives a brownish-green color with ferric chloride.

Anal. Calcd. for $C_{13}H_{13}O_6Br$: C, 45.21; H, 3.76. Found: C, 45.21; H, 3.97.

The Kurt Meyer titration methods were used to determine whether the substance is an enol or a keto form. The yellow solid was dissolved in a mixture of chloroform and absolute alcohol and titrated at −5° with a standard alcoholic bromine solution. The value of this freshly prepared solution was found immediately before and after the titration and its mean value used; the time required for the whole determination was less than three minutes. Two determinations gave 103 and 91% enol, the lack of agreement being due to the difficulty of being sure of the end-point of the reaction. The indirect titration method was also used; excess of bromine was added to the dissolved substance at −5°, the excess decolorized with β-naphthol and the iodine set free from potassium iodide titrated with standard sodium thiosulfate solution. The end-point was difficult to obtain with the accuracy usually possible in this method because instead of obtaining a colorless solution on disappearance of free iodine, a faintly yellow colored solution was left due to the brilliant yellow color of the ester. It was for this reason that the direct method was tried but it was found that after several trials the end-point in the indirect method could be judged so that the error was not more than 5%. This method indicated that the ester is 100% enol.

Methyl α,α-Dimethoxy-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2BrCOCH_2C(OCH_3)_2CO_2CH_3$, II.—Four g. of the dibromo ester suspended in 30 cc. of methyl alcohol was treated with two molecular equivalents of sodium methylate (0.4 g. of sodium in 10 cc. of methyl alcohol) and the solution heated for five minutes on a steam-bath. No crystals formed as the solution cooled so ice was added and the precipitated solid was filtered off, washed and dried; it separated in heavy needles which melted at 128° after two recrystallizations from methyl alcohol.

Anal. Calcd. for $C_{15}H_{19}O_7Br$: C, 46.03; H, 4.85. Found: C, 46.11; H, 4.81.

This dimethoxy ester was the only product of reaction except for 0.3 g. of acid obtained by acidifying the aqueous filtrate and later identified as a mixture of the acid corresponding to this ester and a trace of a yellow acid. The ester does not decolorize a potassium permanganate solution nor does it react with bromine at 0°; it reacts, however, with bromine at room temperature with elimination of hydrogen bromide and gives the same unsaturated bromo ester (123°) that was obtained by recrystallizing the dibromomethoxy ester (96°). The dimethoxy ester is not hydrolyzed by boiling glacial acetic acid; when finely powdered and left in contact with concd. hydrochloric acid for one hour, half of it was recovered unchanged and the other half was hydrolyzed to give the enol ester (168°) obtained from the unsaturated methoxy ester.

α,α-Dimethoxy-5-bromo-2,4-dimethoxybenzoylpropionic Acid, $(CH_3O)_2C_6H_2BrCOCH_2C(OCH_3)_2CO_2H$, III, and α-Hydroxy-5-bromo-2,4-dimethoxybenzoylacrylic Acid, $(CH_3O)_2C_6H_2BrCOCH{=}COHCO_2H$, V.—The dimethoxy acid is obtained mixed with a small quantity of a yellow acid when the dibromo ester is heated for one hour with a large excess of sodium methylate; 4 g. of dibromo ester, in 60 cc. of boiling methyl alcohol, was heated with sodium methylate (0.6 g. of sodium in 20 cc. of methyl alcohol) on a steam-bath for one hour. Solid did not separate when the solution was cooled nor when ice was added but hydrochloric acid precipitated a white powder which was filtered off, washed and dried; 2.7 g. of product melting at 144° was obtained. It was purified by recrystallization from chloroform, from which it separates in transparent cubes melting at 152°. A second acid was isolated in small quantity from the chloroform filtrates; it crystallizes from chloroform, methyl alcohol and benzene in fine yellow needles melting at 179° with rapid decomposition.

Anal. (152°) Calcd. for $C_{14}H_{17}O_7Br$: C, 44.56; H, 4.50; CH_3O, 32.89. Found: C, 44.63, 44.70; H, 4.42, 4.24; CH_3O, 32.39.

Anal. (179°) Calcd. for $C_{12}H_{10}O_6Br$: C, 43.50; H, 3.32; CH_3O, 18.73. Found: C, 43.24; H, 3.30; CH_3O, 18.76, 18.25.

The acid (152°) was suspended in ether solution and treated with an ether solution of diazomethane; evaporation of the solvent left the calculated quantity of the dimethoxy ester (128°). This proves that the latter is the ester of the acid (152°).

The dimethoxy acid is changed quickly and completely into the hydroxy acid (179°) by dissolving it in boiling glacial acetic acid; its behavior is, therefore, different from that of both the unsaturated methoxy ester (157°) and the dimethoxy ester (128°) which are not changed by boiling for several hours with glacial acetic acid. Boiling the dimethoxy acid with acetic acid must be avoided because the hydroxy acid which is formed reacts with glacial acetic acid.

In all the reactions with the dibromo ester and sodium methylate a small quantity of the hydroxy acid (179°) was always obtained after acidifying the aqueous solution, even when the methyl alcohol used was dried with extreme care. It is difficult to separate this acid completely from the dimethoxy acid which is precipitated with it but it can be obtained in any quantity desired by hydrolysis of the dimethoxy acid which is readily prepared.

The yellow acid (179°), suspended in chloroform, reacts quickly at 0° with the calculated quantity of bromine; elimination of hydrogen bromide begins at once and a colorless solid separates from the chloroform. It was washed with 50% acetic acid and then with ether, which left a chalk-white powder melting at 170°; yield, 90–95%.

Anal. Calcd. for $C_{12}H_{10}O_6Br_2$: C, 35.12; H, 2.43. Found: C, 35.27; H, 2.51.

Methyl α-Methoxy-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2CH_3$, VIII.—The acid (179°) was suspended in absolute ether and treated with an absolute ether solution of diazomethane; a rapid reaction took place and a new bright yellow solid was formed. A mixed melting point proved that it was the same substance (168°) which was obtained by treatment of both the unsaturated methoxy ester (157°) and the dimethoxy ester (128°) with hydrochloric acid; it is the ester of the hydroxy acid $(CH_3O)_2C_6H_2BrCOCH{=}COHCO_2CH_3$, IX. This yellow ester, left in absolute ether with excess of diazomethane, gradually disappeared and evaporation of the ether left a colorless product, extremely soluble in organic solvents. It was recrystallized twice from methyl alcohol, from which it separated in feathery white needles melting at 113°.

Anal. Calcd. for $C_{14}H_{15}O_6Br$: C, 46.79; H, 4.17. Found: C, 47.01; H, 4.13.

This ester is formed quickly and in quantitative yield if the hydroxy acid is dissolved in a mixture of chloroform and methyl alcohol and treated with diazomethane. It reacts with bromine at 0° to give the same dibromo ester (96°) as the unsaturated methoxy ester (157°) and this dibromo ester gives the unsaturated bromomethoxy ester (123") on recrystallization. The ester (113') is therefore the geometrical isomer of the ester (157°).

The Kurt Meyer direct and indirect titration methods were applied, as described in the work with the yellow ester (168°), to a study of the yellow acid (179°); the following results were obtained: direct titration, 95, 97% of enol; indirect titration, 95, 94, 95, 102% of enol. The substance is therefore an enol or it enolizes rapidly at —5 to 0°.

Reaction of the Dibromo Methyl Ester in Methyl Alcohol Solution Containing Aqueous Potassium Hydroxide

A solution of 6 g. of the dibromo ester in 90 cc. of boiling methyl alcohol was heated with 3.6 cc. of potassium hydroxide solution (11 g. in 25 cc. of H_2O) for thirty minutes on a steam-bath, cooled in ice and the precipitated solid filtered off; yield 3.1 g. melting at 120–135'. Ice was added to the filtrate and the solution was extracted with ether; evaporation of the ether left 1 g. of the same mixture (120–138°). Treatment of the aqueous solution with hydrochloric acid precipitated a yellow solid. 0.2 g., which was separated into two acids by taking advantage of the lack of solubility of one of them in hot methyl alcohol. The acid left was an almost colorless powder melting at 202° and the acid which crystallized from the solution in brilliant yellow needles melted at 179° when pure. It is the acid V. From the 4.1 g. of mixture (120–138") 1.4 g. of the ester I melting at 157° was separated by warming the mixture with carbon disulfide and crystallizing the residue from methyl alcohol; the rest was a mixture which contained some dibromo ester but it was not found possible to make a complete separation of it even after accumulating a large quantity of material. Not a trace of the ester (113°) could be found. The acid 202° is the only one of the products which is not formed in the reaction of the dibromo ester and sodium methylate; it is α-methoxy-5-bromo-2,4-dimethoxybenzoylacrylic acid, IV, which was later obtained from the reaction between dibromobromodimethoxybenzoylpropionic acid and methyl alcoholic potassium hydroxide. (See p. 1490.)

The unsaturated bromo ester (139°) was heated for a few minutes with a methyl alcohol solution of potash; the dimethoxy acid (152') and the hydroxy acid (179') were the only products formed. These same substances were obtained by treating the unsaturated methoxy ester (157') in the same way. This may indicate that the methoxy ester is an intermediate product in the reactions in which these two acids are formed.

Reactions with the Dibromo Ethyl Ester

Ethyl α,β-Dibromo-5-bromo-2,4-dimethoxybenzoylpropionate, $(CH_3O)_2C_6H_2Br$-$COCHBrCHBrCO_2C_2H_5$.—A mixture of racemic isomers was obtained on bromination of the unsaturated ethyl ester; the lower melting one (141°) which is about 80% of the crude product was separated after several recrystallizations from alcohol. The residue in both alcohol and dilute acetic acid solutions deposits two kinds of crystals, opaque rosets and transparent stars, which can be picked apart. Mechanical separation followed by recrystallization from alcohol gave a small quantity of the isomer (160–161°).

A d . Calcd. for $C_{14}H_{15}O_5Br_3$: C, 33.39; H, 2.98. Found: I (141°) C, 33.31; H, 2.94. II (160–161"): C, 33.71; H, 3.20.

Two isomeric unsaturated esters are formed when the dibromo esters are heated with potassium acetate; the higher melting one (144°) is yellow and is transformed in the sunlight into the lower melting, colorless isomer (114°); yield of pure substances, 77%.

Anal. Calcd. for $C_{14}H_{14}O_5Br_2$: C, 39.81; H, 3.31. Found: I (144°) C, 39.99; H, 3.05. I1 (114"): C, 40.06; H, 3.46.

Ethyl *α*-Ethoxy-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH{=}COC_2H_5CO_2C_2H_5$, **and Ethyl *α,α*-Diethoxy-5-bromo-2,4-dimethoxybenzoylpropionate,** $(CH_3O)_2C_6H_2BrCOCH_2C(OC_2H_5)_2CO_2C_2H_5$.—A solution of 3 g. of dibromo ethyl ester in 25 cc. of absolute alcohol was boiled for fifteen minutes with sodium ethylate (0.3 g. of sodium in 10 cc. of absolute alcohol), the solution cooled and the crystalline solid filtered off, washed and dried; one g. of pure ester was separated after two recrystallizations from alcohol and chloroform. It separates in asbestos-like crystals which melt at 162". Ice was added to the filtrate and the precipitated solid was purified with alcohol as a solvent; one g. of thick needles melting at 132° was obtained.

Anal. (162°) Calcd. for $C_{16}H_{19}O_6Br$: C, 49.61; H, 4.90. Found: C, 49.81; H, 4.91.

Anal. (132°) Calcd. for $C_{18}H_{25}O_7Br$: C, 49.88; H, 5.77. Found: C, 49.64; H, 5.68.

Treatment of the aqueous filtrate with hydrochloric acid precipitated 0.1 g. of the unsaturated hydroxy acid (179°).

The diethoxy ester can be prepared free from the unsaturated ethoxy ester if the reaction is carried out with an excess of sodium ethylate. From 3 g. of dibromo ester treated with 0.9 g. of sodium, 1 g. of diethoxy ester was obtained and 1.2 g. of unsaturated hydroxy acid (179°). When the reaction was carried out in absolutely dry apparatus with alcohol that had been distilled twice over calcium only a trace of this acid was formed.

The reaction with the dibromo ethyl ester and sodium ethylate was repeated under a variety of conditions in an attempt to prepare the diethoxy acid, but it is not formed. This was unexpected in view of the ease with which the corresponding dimethoxy acid is formed. Hydrolysis of the diethoxy ester with alkalies gives only the unsaturated hydroxy acid.

When the unsaturated ethoxy acid was treated in absolute alcohol solution with sodium ethylate, the products formed were the diethoxy ester and the hydroxy acid; with alcoholic potassium hydroxide the hydroxy acid is the only product. These reactions indicate a possible mechanism for the formation of the three products obtained from the dibromo ethyl ester.

Ethyl *α*-Hydroxy-5-bromo-2,4-dimethoxybenzoylacrylate, $(CH_3O)_2C_6H_2BrCOCH{=}COHCO_2C_2H_5$.—The unsaturated ethoxy ester and the diethoxy ester are hydrolyzed by concd. hydrochloric acid but much less readily than the corresponding methoxy esters. The hydroxy ester can be separated from the hydroxy acid, which is formed in small quantity by boiling the mixture of solids with water which dissolves the acid and leaves the ester undissolved; the ester was recrystallized from alcohol from which it separates in feathery yellow needles melting at 143°.

Anal. Calcd. for $C_{14}H_{15}O_6Br$: C, 46.78; H, 4.17. Found: C, 46.49; H, 4.11.

The substance gives a brownish-green color with ferric chloride and an olive green compound on treatment in ether solution with copper acetate.

Anal. Calcd. for $C_{14}H_{14}O_6Br\frac{1}{2}Cu$: Cu, 8.13. Found: Cu, 8.53.

Reactions with the Dibromo Acid

α,β-Dibromo-5-bromo-2,4-dimethoxybenzoylpropionic Acid, $(CH_3O)_2C_6H_2Br$-$COCHBrCHBrCO_2H$.—The unsaturated acid gave a quantitative yield of dibromo acid when brominated in chloroform solution; the substance separates from chloroform with solvent of crystallization (m. p. 177.5°) which it loses gradually, leaving a powder melting at 184.5°. It can also be recrystallized from methyl and ethyl alcohol.

Anal. Calcd. for $C_{12}H_{11}O_5Br_3$: C, 30.31; H, 2.31. Found: C, 30.65; 30.59; H, 2.20. 2.30.

α or β-Bromo-5-bromo-2,4-dimethoxybenzoylacrylic Acid, $(CH_3O)_2C_6H_2BrCOCH{=}CBrCO_2H$ or $(CH_3O)_2C_6H_2BrCOCBr{=}CHCO_2H$.—A solution of 9 g. of dibromo acid in 40 cc. of glacial acetic acid was heated with 13.5 *g.* of potassium acetate for fifteen minutes, the solution cooled and the precipitate washed with 50% acetic acid until colorless; m. p. 178–180°. After removal of a small quantity of the same substance from the aqueous solution, it was treated with hydrochloric acid, which precipitated a yellow solid. This separates from methyl alcohol in fine yellow needles melting at 200°; it is transformed by the sunlight into a colorless solid which melts at 182° and is the isomeric acid which separated first from the acetic acid solution. The colorless isomer can be recrystallized from chloroform or 50% acetic acid.

Anal. Calcd. for $C_{12}H_{10}O_5Br_2$: C, 36.54; H, 2.53. Found: I (200°) C, 36.60; H, 2.65. II (182°): C, 36.50; H, 2.50.

These geometrical isomers are also obtained from the reaction between the dibromo acid and sodium methylate and they are the only products formed; in one reaction the yellow acid (200") was separated in small quantity when the dibromo acid was heated in methyl alcohol solution with aqueous potassium hydroxide.

α-Methoxy-5-bromo-2,4-dimethoxybenzoylacrylic Acid and a-Ethoxy-5-bromo-2,4-dimethoxybenzoylacrylic Acid, $(CH_3O)_2C_6H_2BrCOCH{=}COCH_3CO_2H$ and $(CH_3O)_2$-$C_6H_2BrCOCH{=}COC_2H_5CO_2H$.—The reaction between the dibromo acid in methyl and ethyl alcohol solution with potassium hydroxide gives intractable oils unless it is controlled carefully, and even then the yield of unsaturated alkoxyl acids is very small. The acids are decomposed by recrystallization from chloroform or benzene, so that the usual method of purification was not applied. The dibromo acid was dissolved in methyl or ethyl alcohol, a few drops of aqueous potassium hydroxide (14.5 *g.* in 35 cc. of water) added and the mixture allowed to stand at room temperature for five minutes. Ice was added and the solution made acid with acetic acid; a solid was precipitated which can be purified by washing with methyl or ethyl alcohol or by solution in sodium carbonate and reprecipitation with acetic acid. Both acids are faintly yellow powders; the methoxy acid melts at 202° and the ethoxy acid at 197°.

Anal. (202°) Calcd. for $C_{13}H_{13}O_6Br$: C, 45.21; H, 3.76. Found: C, 46.61; H, **3.86.**

Anal. (197°) Calcd. for $C_{14}H_{15}O_6Br$: C, 46.78; H, 4.17. Found: C, 47.03; H, 4.10.

The filtrates left after removal of the alkoxy acids gave on acidification with hydrochloric acid small quantities of the unsaturated hydroxy acid (179°).

Summary

The reaction of the dibromo methyl ester of 5-bromo-2,4-dimethoxybenzoylacrylic acid with sodium methylate can be controlled so that any one of three methoxy compounds is the chief product, mixed with a small quantity of a yellow hydroxy acid. These methoxy and hydroxy com-

pounds are probably a result of addition to the bromodimethoxybenzoylpropiolic ester formed by loss of two molecules of hydrogen bromide from the dibromo ester. This acetylenic ester has not been isolated but two intermediate ethylenic bromo esters have been prepared and shown to give two of the products obtained from the dibromo ester. The reaction of this dibromo methyl ester with methyl alcoholic potash has also been studied.

The dibromo ethyl ester gives with sodium ethylate products corresponding to all those obtained from the methyl ester with one exception but the dibromo acid is unreactive compared with its esters and loses only one molecule of hydrogen bromide on treatment with sodium methylate, forming isomeric ethylenic bromo acids. With potash the dibromo acid gives products which are a result of addition to bromodimethoxybenzoylpropiolic acid,

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THE REACTION OF THE GRIGNARD REAGENT WITH γ-CHLOROPROPYL PARA-TOLUENESULFONATE. A METHOD OF LENGTHENING CARBON CHAINS BY THREE CARBON ATOMS

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In synthetic organic work it is often necessary to build up the higher homologs of any series of compounds from the lower ones. Recently the practice of increasing carbon chains by one or two methylene groups by use of the Grignard reagent and formaldehyde or ethylene oxide, respectively, has become fairly common and laboratory details for these methods are available.[1] Gilman and Beaber[2] have published a preliminary paper on the reaction of the Grignard reagent with halogenated alkyl esters of aryl sulfonic acids in which they mention the possibility of the practical use of this reaction for the lengthening of the carbon chain in alkyl halides according to the following equation: $CH_3C_6H_4SO_2O(CH_2)_xCl + RMgX \longrightarrow R(CH_2)_xCl + CH_3C_6H_4SO_2OMgX$. Most of the work reported in this paper dealt with β-chloro-ethyl p-toluenesulfonate, but one reaction using γ-chloropropyl p-toluenesulfonate was recorded. While the yields reported in this preliminary work were not exceptionally good, the reaction seemed worthy of further study.[3]

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[1] "Organic Syntheses," 6, 22, 54 (1926).

[2] Gilman and Beaber, THIS JOURNAL, 45,839 (1923).

[3] Before beginning this study, we were informed by Dr. Gilman that he did not expect to extend his researches on this particular reaction and that he did not object to our undertaking a further study of it.

Since the reaction of the Grignard reagent with ethylene oxide runs rather smoothly to give the primary alcohol with two more methylene groups, we have confined our attention mainly to the reaction of the Grignard reagent with y-chloropropyl p-toluenesulfonate in the hope of obtaining a practical method of increasing the chain by three methylene groups.

In preliminary experiments using equimolecular proportions of the Grignard reagent (RMgX) and y-chloropropyl p-toluenesulfonate, the expected product ($R(CH_2)_3Cl$) was obtained in approximately the same yields that Gilman has reported in similar reactions between other alkyl sulfonates and the Grignard reagent. However, there were obtained as by-products in these experiments the dihalogen derivative $X(CH_2)_3Cl$ (where X is the halogen of the Grignard reagent) and the hydrocarbon RH (where R is the hydrocarbon group of the Grignard reagent).

The simplest reactions which suggest themselves as a satisfactory explanation[4] of these products are as follows

$$CH_3C_6H_4SO_2O(CH_2)_3Cl + RMgX \longrightarrow R(CH_2)_3Cl + CH_3C_6H_4SO_2OMgX \quad (1)$$

$$CH_3C_6H_4SO_2O(CH_2)_3Cl + RMgX \longrightarrow X(CH_2)_3Cl + CH_3C_6H_4SO_2OMgR \quad (2)$$

$$CH_3C_6H_4SO_2OMgR + Hz0 \longrightarrow CH_3C_6H_4SO_2OMgOH + RH \quad (3)$$

It was thought that if the reaction represented by Equation 2 actually took place, the compound[6] $CH_3C_6H_4SO_2OMgR$ might be expected to react with another molecule of the chloropropyl ester as follows

$$CH_3C_6H_4SO_2O(CH_2)_3Cl + CH_3C_6H_4SO_2OMgR \longrightarrow (CH_3C_6H_4SO_2O)_2Mg + R(CH_2)_3Cl \quad (4)$$

With this in mind the proportions used in the reaction were changed and two molecules of the chloropropyl ester were used to one of the Grignard reagent. With this change in the procedure the reaction becomes a useful synthetic process, as the yields obtained are usually about 50% of the theoretical amount when the higher alkyl magnesium halides are used.

A double decomposition similar to that represented by Equation 2 takes place when simple alkyl esters of p-toluenesulfonic acid react with the Grignard reagent. Thus when butyl p-toluenesulfonate reacts with one mole of benzylmagnesium chloride, the reaction products include n-amyl benzene (previously reported by Gilman and Beaber),[6] n-butyl chloride and toluene.

Gilman and Beaber[7] have reported that the lower alkyl magnesium halides do not react with the alkyl p-toluenesulfonates to give good yields of the expected products. This observation has been confirmed in the

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[4] Since this paper was written Gilman and Heck have advanced a much simpler explanation for these reactions. (Private communication.)

[5] This type of compound has been formulated before by Kenyon, Phillips and Turley, J. *Chem. Soc.*, 127,402 (1925).

[6] Gilman and Beaber, THIS JOURNAL, 47,523 (1925).

[7] Ref. 6, p. 519.

reaction of ethylmagnesium bromide and n-butylmagnesium bromide with γ-chloropropyl *p*-toluenesulfonate. As by-products in these reactions, certain unidentified volatile sulfur compounds are formed. A yield of 23% of n-amyl chloride was obtained from ethylmagnesium bromide. The exact yield of heptyl chloride from the n-butyl Grignard reagent was not determined on account of the difficulties of separating a pure product.

High boiling products which do not hydrolyze with alkali are sometimes formed and these indicate the possibility of some formation of sulfones. The amounts of these products thus far obtained are not sufficient for their isolation in pure condition and identification.

From the results thus far obtained, this method of lengthening carbon chains by three methylene groups is satisfactory when a Grignard reagent with six or more carbon atoms is used as the starting material.

Experimental Part

γ-Chloropropyl *p*-Toluenesulfonate.[8]—A mixture of 210 g. (1.1 moles) of *p*-toluenesulfonyl chloride and 189 g. (2 moles) of trimethylene chlorohydrin was placed in a 3-liter, three-necked flask fitted with a mechanical stirrer, a separatory funnel and a thermometer. The flask was placed in an ice-water bath and stirring was started. When the temperature had dropped to about 8°, the addition of 320 cc. of 5 *N* sodium hydroxide solution through the separatory funnel was begun. The rate of addition was regulated to maintain the temperature between 8 and 15°. Stirring was continued for about an hour after the addition of the alkali. Then a second portion of 210 g. of p-toluenesulfonyl chloride was introduced into the mixture and a second 320 cc. of 5 N sodium hydroxide solution was added as before. Stirring was continued for about three hours after the addition of the last of the alkali. The ester was extracted with ether and the ether layer was washed with water, then with a little 20% sodium hydroxide and was finally dried over anhydrous potassium carbonate. The ether was distilled at ordinary pressure and the residue under reduced pressure. The ester boiled at 188–192° at 5 mm. The yield varied from 248–275 g. (50–55% of the theoretical amount).

The ester has been prepared before by Gilman and Beaber[8] who report the following physical constants: d_4^{20}, 1.2674; n_D^{20}, 1.5230; b. p. 216–217° (17 mm.). Our product had the following constants: sp. gr. $\frac{25}{25}$, 1.2396; n_D^{21}, 1.5225; and b. p. 188–192° at 5 mm. In some cases the ester was obtained as a semi-solid but it never completely crystallized.

Anal. Subs., 0.6543: $BaSO_4$, 0.6009. Calcd. for $C_{10}H_{13}SO_3Cl$: S, 12.86. Found: S, 12.60.

Reaction of One Mole of the Grignard Reagent with One Mole of **γ-Chloropropyl *p*-Toluenesulfonate.**—The Grignard reagent was prepared in the usual manner in a three-necked flask of suitable size, which was fitted with a separatory funnel, mechanical stirrer and reflux condenser. The chloro ester was then added at such a rate that the ether refluxed gently. Preliminary experiments seemed to indicate that there was no change in yields at different reaction temperatures. The reaction mixture was stirred and maintained at gently boiling temperature for about eight hours after the addition of the last of the chloro ester. Additional ether was added from time to time in order to keep the mixture fluid enough for efficient stirring.

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[8] This method is based on the method for n-butyl p-toluenesulfonate by Gilman and Beaber. Private communication.

[9] Ref. 2, p. 842.

The reaction mixture was then decomposed with cracked ice and treated with enough dilute hydrochloric acid to dissolve the basic magnesium salts. The ether layer was separated, the water layer extracted with ether and the extract combined with the original ether solution. The ether solution was then carefully distilled with a fractionating column. When ethylmagnesium bromide and *n*-butylmagnesium bromides were the Grignard reagents used, the lower boiling fractions obtained in this distillation had the very disagreeable odor that is characteristic of the volatile sulfur compounds. When these fractions were washed with cold concd. sulfuric acid the material which carried this odor was dissolved and pure halogen derivatives could be obtained by fractionation of the insoluble material.

On pouring the sulfuric acid which was used for the purification onto crushed ice a few cc. of a substance with a very disagreeable odor was obtained. Not enough of this material was isolated for identification.

The reactions studied and the products isolated are described in Table I. In every case a gram molecule of the alkyl halide and equivalent amounts of magnesium and y-chloropropyl *p*-toluenesulfonate were used. The amount of ether used for the preparation of the Grignard reagent was 300–400 cc. but as mentioned before more ether was added to the reaction mixture as it was needed.

TABLE I

PRODUCTS OBTAINED BY THE REACTION OF ONE MOLE OF RMgX WITH ONE MOLE OF γ-CHLOROPROPYL *p*-TOLUENESULFONATE

						Physical constants	
Alkyl halide	Amt., *g.*	Products isolated	Wt., *g.*	Yield, %	B. p., °C.	Sp. gr., $\frac{25}{25}$	n_D^{25}
n-C_4H_9Cl	93	$Cl(CH_2)_3Cl$	27	..	123–125	1.080	1.4362
n-C_4H_9Br	137	$Cl(CH_2)_3Br$	50	..	138–140	1.4718	1.4732
n-C_4H_9I	184	$Cl(CH_2)_3I$ (not pure)	60	..	47–59 at 6 mm.	1.6703	1.6312
n-$C_7H_{15}Br$	179	$Cl(CH_2)_3Br$	63	..	138–140	....	....
		$C_7H_{15}(CH_2)_3Cl$	20	11.4	137–142 at 24 mm.	0.8850	1.4400
$C_6H_{11}Br$	163	$Cl(CH_2)_3Br$	73	..	138–140	....	....
		$C_6H_{11}(CH_2)_3Cl$[a]	24	14	76–79 at 5 mm.	0.9977	1.4660
$C_6H_5CH_2Cl$	127	$Cl(CH_2)_3Cl + C_6H_5CH_3$[b]	34	..	114–120	....	....
		$C_6H_5(CH_2)_4Cl$	72	42	98–102 at 6 mm.	1.0295	1.5183
$C_6H_5(CH_2)_4Cl$	169	$Cl(CH_2)_3Cl$	36	..	123–125	....	....
		$C_6H_5(CH_2)_3CH_3$	50	..	178–180	0.8754	1.4920
		$C_6H_5(CH_2)_7Cl$[c]	53	25	131–136 at 6 mm.	0.9899	1.5152

[a] And. Subs., 0.2100: 13.1 cc. of 0.1001 N $AgNO_3$. Calcd. for $C_9H_{17}Cl$: Cl, 22.14. Found: Cl, 22.09.

[b] This mixture could not be separated by fractional distillation. The odor of each of the constituents was apparent. The toluene was identified by conversion to benzoic acid. A mixture of equimolecular amounts of these two constituents was prepared and its boiling point and density agreed with that of the mixture isolated in this experiment.

[c] *Anal.* Subs., 0.2090: 9.6 cc. of 0.1010 N $AgNO_3$. Calcd. for $C_{13}H_{19}Cl$: Cl, 16.8. Found: Cl, 16.4.

It will be noted that no heptyl chloride was isolated when the butylmagnesium halides were used. Volatile sulfur compounds were produced rather abundantly in these experiments.

Reaction of One Mole of the Grignard Reagent with Two Moles of γ-Chloropropyl *p*-Toluenesulfonate.—These reactions were run exactly as described in the preceding experiments with the exception that two equivalents of the ester were used for one equivalent of the Grignard reagent. No hydrocarbons were isolated except in one case. A high boiling residue of unchanged ester was recovered in a few cases. This indicates that in certain cases less than two moles of ester could be used with as good yields of final product. The results of these experiments are collected in Table II.

TABLE II

PRODUCTS OBTAINED BY THE REACTION OF ONE MOLE OF RMgX WITH TWO MOLES OF γ-CHLOROPROPYL *p*-TOLUENESULFONATE

						Physical *properties*	
Alkyl *halide*	Amt., *g.*	*Products isolated*	Wt., g.	*Yield*, %	*B. p.*, °C.	Sp. gr. $\frac{25}{25}$	n_D^{25}
$C_6H_5CH_2Cl$	127	$Cl(CH_2)_3Cl$	50	..	123–125	1.080	1.4362
		$C_6H_5(CH_2)_4Cl$	99	50	98–102 at 6 mm.	1.0295	1.5183
C_6H_5Br	157	$Cl(CH_2)_3Br$	51	..	138–140	1.4718	1.4732
		$C_6H_5(CH_2)_3Cl$	93	62	89–93 at 6 mm.	1.0801	1.5160
C_2H_5Br	109	$Cl(CH_2)_3Br$	100	..	138–140	....	....
		$C_2H_5(CH_2)_3Cl$	25	23	106–108	0.8890	....
n-$C_6H_{13}Br$	165	$Cl(CH_2)_3Br$	100	..	138–140	....	....
		$C_6H_{13}(CH_2)_3Cl$	83	52	76–79 at 4 mm.	0.8931	1.4400
n-$C_{12}H_{25}Br$	55	$Cl(CH_2)_3Br$	33	..	138–140	....	....
		$C_{12}H_{25}(CH_2)_3Cl$	20	30[a]	119–121 at 6 mm.	0.8433	1.4470
$C_6H_{11}Br$	163	$Cl(CH_2)_3Br$	98	..	138–140	....	....
		$C_6H_{11}(CH_2)_3Cl$	100	62	76–79 at 5 mm.	0.9977	1.4660
$C_6H_5(CH_2)_4Cl$	173	$Cl(CH_2)_3Cl$	60	..	123–125	....	....
		$C_6H_5(CH_2)_7Cl$	62	44[b]	131–136 at 6 mm.	0.9899	1.5152
		$C_6H_5(CH_2)_3CH_3$	28	..	178–180	0.8754	1.4920
$C_7H_{15}Br$	179	$Cl(CH_2)_3Br$	101	..	138–140	....	....
		$C_7H_{15}(CH_2)_3Cl$	87	50	137–142 at 24 mm.	0.8850	1.4400

[a] The lower yield in this case is due in part to the fact that smaller quantities were used and mechanical losses lowered the yield and in part to the fact that the Grignard reagent is formed in only about 70% yield from lauryl bromide. The yield of pentadecyl chloride based on the Grignard reagent is about 42%.

[b] This yield is based on the actual amount of Grignard reagent used as determined by titration with standard acid.

Benzylmagnesium Chloride and n-Butyl *p*-Toluenesulfonate.—When one mole of benzylmagnesium chloride and one mole of n-butyl *p*-toluenesulfonate were allowed to react according to the method described bv Gilman and Beaber,[4] careful fractionation of the products showed that 18 g. of n-butyl chloride (b. p. 75–81°), 22 g. of toluene (b. p. 106–112°) and 45 g. of n-amylbenzene (b. p. 198–201°) were obtained.

If the ratio was changed so that one mole of the Grignard reagent reacted with two moles of the ester, the products isolated were 24 g. of n-butyl chloride (b. p. 76–80') and 74 g. of n amylbenzene (b. p. 198–201°).

Summary

1. The reactions of various Grignard reagents with γ-chloropropyl p-toluenesulfonate have been studied.

2. Conditions have been described which make this a useful synthetic reaction in converting RX to $R(CH_2)_3Cl$.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. VIII. THE ACTION OF POTASSIUM HYDROXIDE ON FRUCTOSE

BY WILLIAM LLOYD EVANS AND JAMES EDWIN HUTCHMAN

RECEIVED MARCH 19, 1928 PUBLISHED MAY 5, 1928

It has been shown that temperature and concentration of alkali are experimental factors which exert a marked influence on the quantity of reaction products which may be obtained when glucose, fructose, mannose and galactose are oxidized with potassium permanganate in aqueous solutions of potassium hydroxide.[1] A quantitative study of the reaction products obtained by the action of aqueous solutions of potassium hydroxide on glucose and galactose under definitely chosen conditions of temperature and concentration of the base, and in the absence of potassium permanganate, shows that the equilibrated reacting system is one that is easily disturbed by a change in one or both of these experimental factors.[2] By reason of the fact that fructose in alkaline solutions is converted, in part, to glucose,[3] it became of much interest to know whether this ketohexose would show the same general behavior toward potassium hydroxide as that observed for the aldohexose by Evans, Edgar and Hoff.[2a] To determine this point was the first objective in these experiments.

When fructose-3,4-enediol is ruptured at the double bond, two molecules of the active form of glyceric aldehyde should be formed.[4] Hence, it follows that in those alkaline solutions of the hexoses in which the equilibrium between the enediols has been shifted largely to the 3,4-form, the action of the alkali on the carbohydrate should involve the same general mechanism as that observed by Hass,[5] and Cornthwaite and one of us[6] concerning the behavior of glyceric aldehyde and dihydroxy-acetone

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[1] (a) Evans, Buehler, Looker, Crawford and Holl, THIS JOURNAL, 47, 3085 (1925); (b) Evans and Buehler, *ibid.*, 47, 3098 (1925).

[2] (a) Evans, Edgar and Hoff, *ibid.*, 48, 2665 (1926); see (b) Amick, J. *Phys. Chem.*, 31, 1473–7 (1927); (c) Wolfrom with Lewis, THIS JOURNAL, 50, 838 (1928).

[3] (a) De Bruyn and van Ekenstein, *Rec. trav. chim.*, 14, 156 (1895); (b) 14, 203 (1895); (c) 15, 92 (1896); (d) 16, 257 (1897); (e) 16, 262 (1897); (f) 16, 274 (1897); (g) 19, 1 (1900); (h) 27, 1 (1908).

[4] Ref. 1a, p. 3093.

Evans and Hass, THIS JOURNAL, 48, 2703 (1926).

[6] Evans and Cornthwaite, *ibid.*, 50, 486 (1928).

in aqueous solutions of potassium hydroxide. So establish this predicted similarity of behavior was the second objective in this study.

Experimental Part

Treatment of Fructose with Potassium Hydroxide.—The general methods which have been developed in this Laboratory in a similar study on glucose and galactose[2] were employed in these experiments. To 4.5 g. of *d,l*-fructose contained in a 135-cc. round-bottomed flask, was added 50 cc. of standard potassium hydroxide solution at the temperature of the thermostat. Complete solution was hastened by energetic shaking. The flasks were tightly closed with rubber stoppers and then were agitated for forty-eight hours in a thermostat kept at 25, 50 or 75°. At the end of this period, the flasks were immersed in a freezing mixture for a few minutes, after which the reaction mixtures were treated with equal volumes of standardized phosphoric acid solution of such strength that the resulting solution was neutral. The concentrations of all reacting materials were such that a direct comparison of the experimental results obtained could be made with those of similar work previously published from this Laboratory.

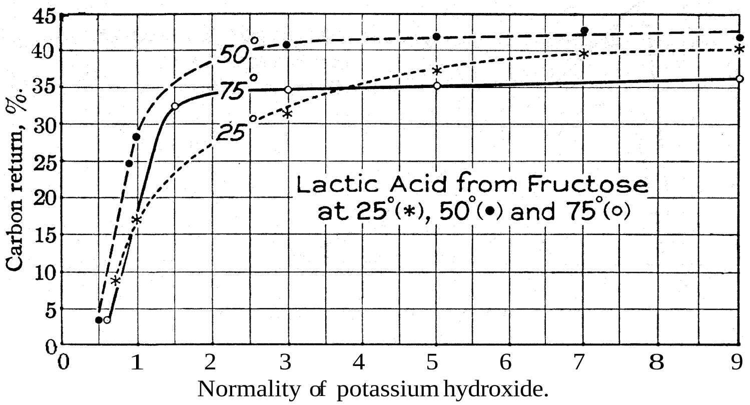

Fig. 1.

Methods of Analysis.—The methods used in the detection and determination of certain reaction products were the same in every detail as those previousy described in previous reports on glucose, galactose,[2] glyceric aldehyde[6] and dihydroxy-acetone.8

Pyruvic Aldehyde **Osazone.—In** the determination of pyruvic aldehyde, samples were made to contain 4.5 g. of fructose in a mixture of 50 cc. of potassium hydroxide solution, 35 cc. of 95% alcohol and 10 cc. of phenylhydrazine in a 125-cc. round-bottomed flask. The temperature of this mixture when the fructose was added was that chosen for the thermostat for that particular experiment. At the end of forty-eight hours, the yellow osazone was filtered, washed with 10 cc. of 30% alcohol and dried at 65° in *vacuo*.

Experimental Data.—The quantitative data obtained in these experiments are shown graphically in Figs. 1, 2, 3, 4, 5 and 6.

Theoretical Part

In a previous report from this Laboratory it was pointed out that certain compounds which were formed by the action of potassium hydroxide on glucose and galactose might be regarded as having been derived from these carbohydrates through the intermediate formation of the isomeric hexose-

1,2-, -2,3- and -3,4-enediols,[2] and that the amounts of these reaction products were functions of both the temperature and the concentration of the base. This point of view is further confirmed in the following discussion of our experimental data.

3,4-Enediol. (a) Lactic Acid.--It has been repeatedly pointed out that the hexose-3,4-enediol in solutions of sufficient alkali concentration will rupture at the double bond, thus giving rise to two molecules of the active form of glyceric aldehyde. This change is shown by the following equation

$$CH_2OHCHOHC(OH){=}C(OH)CHOHCH_2OH \rightleftarrows 2CH_2OHCHOHCH<$$

Under the conditions of these experiments this active glyceric aldehyde may be converted into pyruvic aldehyde, which in turn, is changed into lactic acid. Cornthwaite and one of us[6] have recently shown that the behavior of dihydroxy-acetone and glyceric aldehyde in alkaline solutions is similar to that of aldo- and ketohexoses under similar conditions, that is, these trioses are in equilibrium with their common enediol in the following way

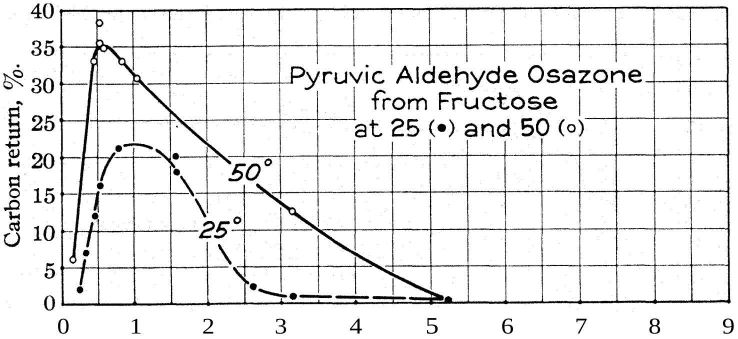

Fig. 2.

$$CH_2OHCHOHCHO \rightleftarrows CH_2OHC(OH){=}CHOH \rightleftarrows CH_2OHCOCH_2OH$$

Since the amounts of lactic acid formed by the action of potassium hydroxide on these two trioses depend on the temperature and the alkali concentration, then it follows that the amounts of lactic acid obtained from a hexose such as fructose and glucose should also show a similar relation to these two experimental factors. That this is true is clearly shown by a comparison of our Pig. 1 with Pig. 1 of Evans and Cornthwaite. This is equally true for glucose.' At 75°, tar formation took place very rapidly, thus causing a decrease in the lactic acid yields. No examination of these tars was made for any possible saccharinic acids.

(b) Pyruvic Aldehyde.--Since the amounts of pyruvic aldehyde ob-

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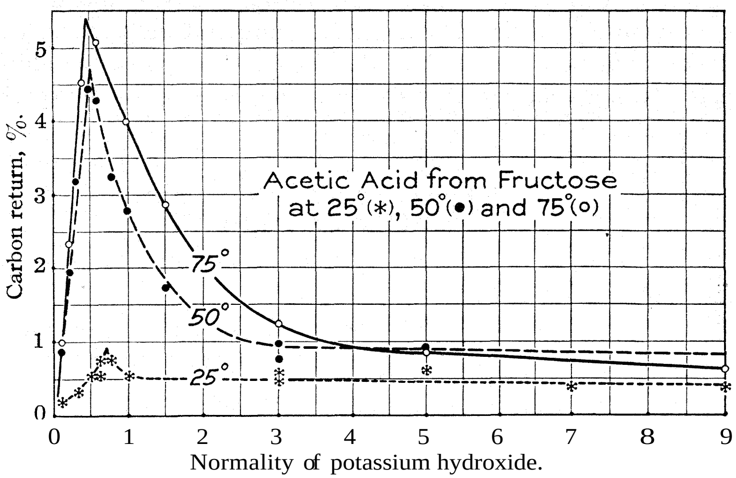
[7] Ref. 2a, p. 2670.

tained from dihydroxy-acetone and glyceric aldehyde depend on the temperature and the alkali concentration, and since the common triose enediol is regarded as an intermediate compound in lactic acid formation, then it follows that the amounts of pyruvic aldehyde obtained from the glyceric aldehyde resulting from the rupture of fructose-3,4-enediol under similar conditions should also show this same general relation to the two variable experimental factors. That this is true may be seen by a comparison of our Fig. 2 and Fig. 2 of Evans and Cornthwaite. This is also true for glucose.[8] It is a very noteworthy fact that the maximum yield of pyruvic aldehyde at a given temperature occurs at approximately the same normality for fructose as that observed for glyceric aldehyde and dihydroxy-acetone; that is, approximately 0.5 N at 50° and approximately 1.0 *N* at 25°. Evans, Edgar and Hoff made the same observation with reference to galactose when this carbohydrate was submitted to exactly the same conditions as the above sugars. In this connection attention should be directed particularly to the fact that the amount of pyruvic aldehyde at the point of maximum yield is different for each carbohydrate studied. This difference at the maxima may be accounted for in the following way. (1) It is well known that glucose, mannose and fructose form equilibria at low alkali concentrations which are qualitatively the same but not quantitatively so.[3] Hence, it would follow that the concentration of the triose formed by the rupture of the fructose-3,4-enediol would be different from that obtained from either glucose or mannose. The equilibrium arising from the interaction of glyceric aldehyde and potassium hydroxide is also not quantitatively identical with that



Pig. 3.

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[8] Ref. 2, p. 2671.

obtained with dihydroxy-acetone at the lower alkali concentrations. (2). The maximum yields of pyruvic aldehyde are always found to be at approximately the same alkali normality as that at which lactic acid formation is first observed. This seems to indicate that pyruvic aldehyde will undergo the benzilic acid rearrangement at only very definite conditions of temperature and hydroxyl-ion concentration, regardless of the concentration of the pyruvic aldehyde. Owing to the fact that the concentration of the glyceric aldehyde obtained from the hexoses must depend on the state of the sugar–alkali equilibrium and the fact that the conversion to lactic acid will only take place under definite conditions, then it is to be expected that the amounts of pyruvic aldehyde obtained at the maxima will be different for the various carbohydrates. On this basis one can safely predict that the maximum point for pyruvic aldehyde from glucose will be different from that of fructose, when the aldohexose is subjected to the same conditions as those employed in these experiments.

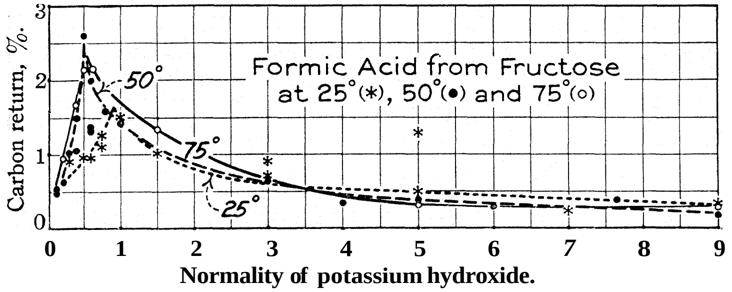

Fig. 4.

(c) Acetic and Formic Acids.—It has been shown previously that the acetic acid and a portion of the formic acid derived from the action of potassium hydroxide on glucose and galactose arise from the action of the alkali upon the decomposition products obtained from pyruvic aldehyde in accordance with the following equation: $CH_3COCHO \longrightarrow CH_3CHO + CO$. When the velocity of the conversion of pyruvic aldehyde to lactic acid becomes greater than that of this decomposition, then it is clear that the yields of these two acids must thereafter diminish. Since this is true for glyceric aldehyde[9] and dihydroxy-acetone,[10] it should also be true for fructose, as is shown in our Figs. 3 and 4. The same general fact was observed previously in the case of both glucose and galactose.

Production Relation of Lactic, Acetic and Formic Acids and **Pyruvic** Aldehyde.—From the above discussion it is clear that the yields of lactic and acetic acids, pyruvic aldehyde and a portion of the formic acid must

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[9] Ref. 5, p. 2711.

[10] Ref. 6, pp. 490, 491.

be closely related, since these compounds are derived from the glyceric aldehyde obtained through the rupture of the fructose-3,4-enediol. This interdependence of the yields of these reaction products is shown in Figs. 5 and 6. A comparison of these two sets of data will show in a very marked manner the effect of temperature on the general reaction. The same general relation has been shown to be true for dihydroxy-acetone at 50° and may be seen to be true for glyceric aldehyde[11] by a comparison of the appropriate data. The practically identical character of this interdependence in the yields of these compounds seems to be very convincing evidence for the proposed general mechanism of the reaction of the hexoses and potassium hydroxide which involves the formation of glyceric aldehyde through a rupture of the hexose-3,4-enediol.

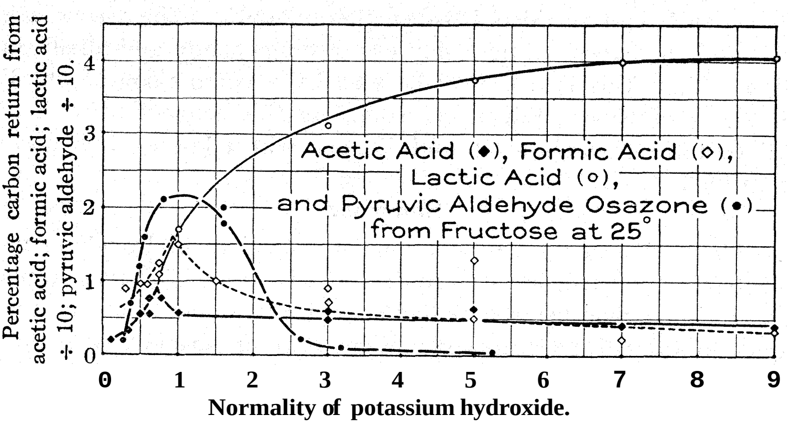


Fig. 5.

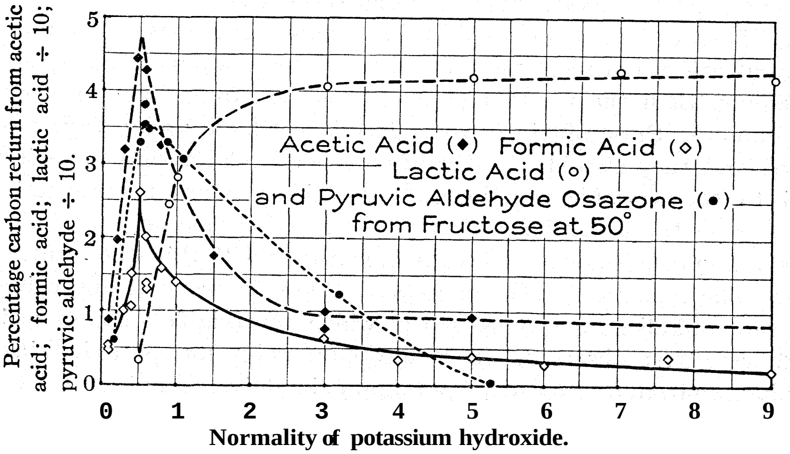


Fig. 6.

[11] Ref. 6, p. 490.

1,2-Enediol. Formic Acid.—All that was previously reported with reference to the glucose-1,2-enediol being a possible source of formic acid in the reaction of potassium hydroxide on glucose, must be equally true for the reaction of the same alkali on fructose, because in both cases the same general relation exists between the amounts of the formic acid obtained and the experimental conditions of temperature and alkali concentration. That this is true may be seen by a comparison of our Fig. 4 with Fig. 4 of Evans, Edgar and Hoff. In this connection it should be noted that the maxima at 50 and 75° occur at a lower alkali normality than at 25°.

Summary

1. The action of aqueous solutions of potassium hydroxide of various concentrations on fructose was studied at 25, 50 and 75° for the purpose of ascertaining whether the character and the amounts of the reaction products obtained under these conditions were in harmony with the commonly accepted views with reference to the presence of equilibrated systems of certain isomeric hexoses and enediols in such solutions. These equilibrated systems should be disturbed by such experimental conditions as temperature and concentration of alkali.

2. Since glucose is one of the carbohydrates formed from fructose in alkaline solutions, then these two hexoses should show the same general relationship to the experimental factors of temperature and concentration of alkali. Our general results show that this is true.

3. If the hexose-3,4-enediols in alkaline solutions of appropriate concentration rupture at the double bond to form two molecules of glyceric aldehyde, then the reaction products obtained from fructose should be the same as those obtained from glyceric aldehyde under similar conditions, and they should bear the same general relationship to each other and to the variable experimental conditions. Our experimental data bearing on the formation of lactic, acetic and formic acids and also the production of pyruvic aldehyde are in harmony with this statement.

4. The maximum yields of pyruvic aldehyde occur at approximately the same alkali normality as that at which appreciable amounts of lactic acid were first observed. This maximum point for pyruvic aldehyde production from fructose at 25° was approximately 1 *N* and at 50° 0.5 *N*. This is also true for glyceric aldehyde, dihydroxy-acetone and galactose.

5. The difference in the maximum yields of pyruvic aldehyde from fructose and glucose should be different by reason of the difference in the concentration of the glyceric aldehyde in each case, which is due in turn to the fact that equilibria in the case of each carbohydrate are not quantitatively identical.

6. Maximum yields of acetic and formic acids are also obtained with fructose as has been observed for glucose. The quantitative differences

are probably due to the differences in the equilibrium conditions noted above.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

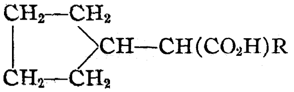
CYCLOPENTYL ALKYL ACETIC ACIDS AND OMEGA-CYCLOPENTYLETHYL ALKYL ACETIC ACIDS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XI[1]

BY G. R. YOHE AND ROGER ADAMS[2]

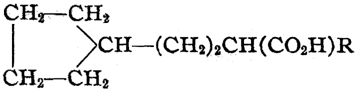
RECEIVED MARCH 26, 1928 PUBLISHED MAY 5, 1928

In previous papers six different isomeric series of acids containing cyclohexyl groups, $C_6H_{11}(CH_2)_xCO_2H$, $C_6H_{11}CH(CO_2H)R$, $C_6H_{11}CH_2CH(CO_2H)R$, $C_6H_{11}(CH_2)_2CH(CO_2H)R$, $C_6H_{11}(CH_2)_3CH(CO_2H)R$, $C_6H_{11}(CH_2)_4CH(CO_2H)R$, have been prepared and have been shown to contain members highly bactericidal in *vitro* to B. Leprae. Those acids with the carboxyl group at the end of the chain were not nearly as effective as the isomers with the carboxyl near the ring. This is a very fortunate circumstance since the latter are much more readily prepared and it is, therefore, possible to make a study of the effect of analogous structures with comparative ease. Acids containing a cyclopentyl group in place of the cyclohexyl group are of interest, not only because they make possible a comparison of the effect of the cyclopentyl and cyclohexyl groups upon the bactericidal activity, but because a cyclopentyl group is present in the dihydrochaulmoogric and dihydrohydnocarpic acids, and the cyclopentenyl group is present in the chaulmoogric and hydnocarpic acids.

In this research two series of acids, cyclopentyl alkyl acetic acids (I) and β-cyclopentylethyl alkyl acetic acids (II) have been prepared,



I



II

where R in (I) was n-heptyl to n-undecyl and R in (II) was ethyl to n-octyl. The bacteriological results are given in Tables I and II.

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[1] For previous articles in this field see (a) Shriner and Adams, THIS JOURNAL, 47, 2727 (1925); (b) Noller with Adams, *ibid.*, 48, 1074 (1926); (c) 48, 1080 (1926); (d) Hiers with Adams, *ibid.*, 48, 1089 (1926); (e) Van Dyke and Adams, *ibid.*, 48, 2393 (1926); (f) Sacks with Adams, *ibid.*, 48, 2395 (1926); (g) Hiers with Adams, *ibid.*, 48, 2385 (1926); (h) Adams, Stanley, Ford and Peterson, *ibid.*, 49, 2934 (1927); (i) Arvin with Adams, *ibid.*, 49, 2940 (1927); (j) Adams, Stanley, and Stearns, *ibid.*, 50, 1475 (1928).

[2] This communication is an abstract of a portion of the thesis submitted by G. R. Yohe in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

TABLE I

BACTERIOLOGICAL TESTS TO B. *Leprae*

Cyclopentyl alkyl acetic acids, $C_5H_9CH(CO_2H)R$

R =	Dilution of sodium salts in thousands 100	111	125	133	143	153	167	176	185	200	250	300
n-C_7H_{15}	*	−	+	+	+	+	+	+	+	+	+	+
n-C_8H_{17}	−	−	+	+	+	+	+	+	+	+	+	+
n-C_9H_{19}	−	−	+	+	±	+	+	+	+	+	+	+
n-$C_{10}H_{21}$	−	−	−	−	−	+	±	±	±	−	+	+
n-$C_{11}H_{23}$	−	−	−	−	−	−	±	±	±	+	+	+

TABLE II

BACTERIOLOGICAL TESTS TO B. *Leprae*

Cyclopentylethyl alkyl acetic acids, $C_5H_9(CH_2)_2CH(CO_2H)R$

R =	Dilution of sodium salts in thousands 10	20	30	40	50	60	700	800	900	100	110	120	130	140	150	160	170	180	190
C_2H_5	−	−	−	+	+	+	+	+	+	+									
n-C_3H_7	−	+	+	+	+	+	+	+	+	+									
n-C_4H_9	−	−	−	+	+	+	+	+	+	+									
n-C_5H_{11}	−	−	−	−	±	−	−	±	+	+									
n-C_6H_{13}	−	−	−	−	−	−	−	−	−	−	−	−	−	±	±	+	+	+	+
n-C_7H_{15}	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	±	+	−
n-C_8H_{17}	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	±	−
$C_5H_9(CH_2)_3CO_2H$	+	+	+	+	+	+	+	+	+	+									
$C_5H_9(CH_2)_4CO_2H$	−	−	−	±	+	+	+	+	+	+									
$C_5H_9(CH_2)_5CO_2H$	−	−	−	±	+	+	+	+	+	+									

As in the cyclohexyl series, the greatest bactericidal action is found in the acids containing sixteen to eighteen carbon atoms. A comparison of the two cyclopentyl series would indicate that the β-cyclopentylethyl alkyl acetic acids are slightly more effective than the isomeric cyclopentyl alkyl acetic acids. A similar slight difference could be detected in the

TABLE III

COMPARISON OR BACTERICIDAL ACTION OR VARIOUS ACIDS

Acids	No.	R =	Maximum bactericidal dilutions in thousands
$C_6H_{11}CH(CO_2H)R$	1a	C_8H_{17}	110
	1b	C_9H_{19}	190
	1c	$C_{10}H_{21}$	180
$C_5H_9CH(CO_2H)R$	2a	C_9H_{19}	111
	2b	$C_{10}H_{21}$	143
	2c	$C_{11}H_{23}$	153
$C_5H_7CH(CO_2H)R$	3a	C_9H_{19}	150
	3b	$C_{10}H_{21}$[a]	167
	3c	$C_{11}H_{23}$[a]	125
$C_6H_{11}(CH_2)_2CH(CO_2H)R$	4a	C_6H_{13}	160
	4b	C_7H_{15}	220
	4c	C_8H_{17}	320
$C_5H_9(CH_2)_2CH(CO_2H)R$	5a	C_7H_{15}	170
	5b	C_8H_{17}	180

[a] These two acids will be described in a subsequent paper in this series.

cyclohexyl series. It is also interesting to note that the cyclopentyl nonyl acetic acid and cyclopentylethyl heptyl acetic acid are isomers of dihydrohydnocarpic acid, and are far more bactericidal than the latter compound.

Comparisons of cyclopentyl with isomeric cyclohexyl compounds and of cyclopentyl with cyclopentenyl compounds are given in Table III. By comparing isomers 1a, 1b, 1c, with 2a, 2b, 2c, and 4a, 4b, with 5a, 5b, it appears that there is no significant difference in bactericidal effect between the cyclohexyl and cyclopentyl compounds of equal molecular weight or of equal length side chain, though the figures appear to favor the cyclohexyl compounds. The difference between 2a, 2b, 2c, and 3a, 3b, 3c, shows the effect of the olefin linkage. It is obvious that the bactericidal action is not affected markedly by the presence of the double bond.

The acids were prepared. by saponification of cyclopentyl alkyl and cyclopentylethyl alkyl malonic esters. The raw material, cyclopentyl bromide, was made from cyclopentanol which, in turn, was made by the catalytic reduction of cyclopentanone. Cyclopentyl ethanol for the second series of compounds was made by the action of ethylene oxide upon cyclopentyl magnesium bromide.

Experimental Part

Cyclopentanol.—This was prepared by the reduction of cyclopentanone by means of hydrogen and platinum-oxide platinum black[3] similar to the procedure described by Noller and Adams,[1e] differing in that 95% ethanol was used as a solvent in place of methanol. A few new observations may be noted about this reaction: (1) catalyst made directly from c. P chloroplatinic acid was not as active as that from reworked catalyst; *(2)* the same catalyst could be used several times, though its activity diminished each time; for example, 0.5 mole of cyclopentanone in 150 cc. of 95% ethanol with 1 g. of catalyst required seven hours for the first reduction, eleven hours for the second and twenty-five hours for the third; (3) in several runs in which relatively small amounts of the solvent alcohol were used (100 cc. of alcohol or less to 1 mole of cyclopentanone) and the platinum oxide was reduced to platinum black in the presence of the ketone, considerable reduction to cyclopentane and water was noted.[4]

Cyclopentyl Bromide.''—From cyclopentanol as previously described. It is preferable to distil this product under diminished pressure, as under ordinary pressure a small amount of decomposition to cyclopentene and hydrogen bromide is sometimes encountered; b. p. 56° at 45 mm.

Cyclopentylethanol.—The same general procedure was used for preparing this as was described by Hiers and Adams[1d] for preparing cyclohexylethanol from cyclohexyl bromide. The only modification was to reflux the reaction mixture for one to two hours after the ethylene oxide had been added to the Grignard solution, then to effect the rearrangement by allowing to stand for one to two days at room temperature. The crude cyclopentylethanol was obtained in 25–35% yields. It was difficult to purify from the ethylene bromohydrin formed as a side product,[5] so the fraction boiling at 85–95° at

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[3] Shriner and Adams, THIS JOURNAL, 45, 2171 (1923); Tuley and Adams, *ibid.*, 47, 3061 (1925).

[4] See Vavon, Compt. rend., 155,287 (1912).

[5] Blaise and Haller, *Compt.* rend., 134, 552 (1902).

22 mm. was converted directly to cyclopentylethyl bromide which could be easily purified.

The pure cyclopentylethanol was prepared by converting the bromide to the acetate and then saponifying with dilute methyl alcoholic potassium hydroxide; b. p. 96.5–97° at 24 mm.; n_{D}^{20}, 1.4577; d_4^{20}, 0.9180. Calcd. for $C_7H_{14}O$: C, 73.66; H, 12.39. Found: C, 73.09; H, 12.18.

β-Cyclopentylethyl Bromide.—From the crude alcohol using the hydrobromic acid and sulfuric acid[6] method, the yields were 60–65%. The phosphorus tribromide method gave essentially the same results; b. p. 75–77° at 19 mm.; n_{D}^{20}, 1.4863; d_4^{20}, 1.2860. Calcd. for $C_7H_{13}Br$: Br, 45.24. Found: 45.30.

Cyclopentylbutanol.—Prepared from cyclopentylethyl bromide in a similar manner to the preparation of cyclopentylethanol from cyclopentyl bromide. Decomposed with 30% sulfuric acid and distilled, the product was readily obtained pure in 70–75% yields; b. p. 88–92° at 2 mm.; n_{D}^{20}, 1.4613; d_4^{20}, 0.9033. Galcd. for $C_9H_{18}O$: C, 75.98; H, 12.77. Found: C, 75.64; H, 12.41.

δ-Cyclopentylbutyl Bromide.—From the alcohol and hydrobromic acid and sulfuric acid.[6] The yield was 60–65%; b. p. 110–111° at 17 mm.; n_{D}^{20}, 1.4820; d_4^{20}, 1.1872. Calcd. for $C_9H_{17}Br$: Br, 38.77. Found: 38.65.

δ-Cyclopentylbutyl Cyanide.—From twenty hours' refluxing of the bromide and 25% excess of potassium cyanide in 75% alcohol, a yield of 80–85% was obtained b. p. 124–126.5° at 17 mm.; n_{D}^{20}, 1.4542; d_4^{20}, 0.8887. Calcd. for $C_{10}H_{17}N$: C, 79.39; H, 11.34. Found: C, 79.33; H, 11.29.

δ-Cyclopentyl Pentanoic Acid.—From twenty-four hours' heating on a steam cone of the cyanide and excess sodium hydroxide in 60% alcohol, a yield of 80–85% was obtained; b. p. 124–128° at 2 mm.; n_{D}^{20}, 1.4594; d_4^{20}, 0.9752. Calcd. for $C_{10}H_{18}O_2$: C, 70.53; H, 10.65. Found: C, 70.21; H, 10.58.

Diethyl δ-Cyclopentylbutyl Malonate.—From the bromide and malonic ester by the usual procedure, a yield of about 40% was obtained; b. p. 154–160° at 2.2 mm.; n_{D}^{20}, 1.4493; d_4^{20}, 0.9934. Calcd. for $C_{16}H_{28}O_4$: C, 67.55; H, 9.93. Found: C, 67.08; H, 9.75.

δ-Cyclopentylbutyl Malonic Acid.—From the ester by the procedure described by Adams, Stanley and Stearns,[1j] a yield of 85% was obtained. From benzene it was readily purified to a m. p. 121–124° (uncorr.). Calcd. for $C_{12}H_{20}O_4$: C, 63.11; H, 8.84. Found: C, 63.10; H, 8.90.

ε-Cyclopentyl Hexanoic Acid.—From the malonic acid by heating for two hours at 160–180°, a yield of 75% was obtained; b. p. 133–135° at 1.8 mm.; m. p. 33–33.5°; n_{D}^{35}, 1.4549; d_4^{35}, 0.9518. Calcd. for $C_{11}H_{20}O_2$: C, 71.68; H, 10.95. Found: C, 71.65; H, 10.83.

Diethyl β-Cyclopentylethyl Alkyl Malonates.—These were all prepared by the usual procedure, condensing β-cyclopentylethyl bromide with the sodium derivatives of the various diethyl alkyl malonates; yields, 50–60%.

Diethyl Cyclopentyl Alkyl Malonates.—Cyclopentyl malonic ester[7] (b. p. 115–117° at 2 mm.; n_{D}^{20}, 1.4440; d_4^{20}, 1.0325) was dissolved in benzene, the calculated amount of sodium dissolved in this solution and the calculated amount of the proper alkyl halide introduced;" yields, 50–60%.

β-Cyclopentylethyl Alkyl Malonic Acids and Cyclopentyl Alkyl Malonic Acids.—These were prepared by heating with excess alcoholic potassium hydroxide overnight and working up as previously described.[1h] All which could not be purified readily were decomposed in crude form to the monobasic acid.

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[6] "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. I, p 1.

[7] Verwey, Ber., 29, 1996 (1896).

β-Cyclopentylethyl Alkyl Acetic Adds **and Cyclopentyl Alkyl** Acetic Acids.—From the malonic acids by heating for two hours at 160–180°, essentially quantitative yields of monobasic acids were obtained.

Alkyl Halides.—Previous articles have described most of those used.[1h] Decyl bromide and undecyl bromide were prepared from the corresponding alcohols and hydrobromic acid and sulfuric acid.[4]

Decyl Alcohol.[8]—From nonyl magnesium bromide and formaldehyde[9] a 60% yield of product was obtained; b. p. 115–120° at 15 mm.

TABLE IV

DIETHYL CYCLOPENTYL ALKYL MALONATES, $C_5H_9C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n_D^{20}	d_4^{20}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
n-C_7H_{15}	143–146 (1 mm.)	1.4548	0.9749	69.88	10.52	69.56	10.23
n-C_8H_{17}	160–165 (1 mm.)	1.4553	.9659	70.53	10.66	70.52	10.67
n-C_9H_{19}	152–155 (0.6 mm.)	1.4567	.9617	71.13	10.81	71.00	10.65
n-$C_{10}H_{21}$	169–171 (1 mm.)	1.4571	.9560	71.68	10.95	71.69	10.88
n-$C_{11}H_{23}$	186–189 (1 mm.)	1.4580	.9522	72.02	11.24	72.38	11.16

TABLE V

DIETHYL β-CYCLOPENTYLETHYL ALKYL MALONATES, $C_5H_9(CH_2)_2C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n_D^{20}	d_4^{20}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
H	125 (2 mm.)	1.4478	1.0082	65.52	9.50	65.39	9.39
C_2H_5	126–129 (1.9 mm.)	1.4511	.9924	67.55	9.93	67.37	9.89
n-C_3H_7	134-135 (1.7 mm.)	1.4510	.9873	68.40	10.14	67.99	10.01
n-C_4H_9	136–140 (1.8 mm.)	1.4523	.9783	69.17	10.33	68.95	10.30
n-C_5H_{11}	148–150 (1.1 mm.)	1.4526	.9688	69.88	10.51	69.71	10.38
n-C_6H_{13}	157–162 (1 mm.)	1.4531	.9624	70.53	10.66	70.42	10.65
n-C_7H_{15}	172–174 (2 mm.)	1.4541	.9563	71.13	10.81	70.91	10.79
n-C_8H_{17}	182–184 (1.2 mm.)	1.4548	.9524	71.68	10.95	71.42	10.97

TABLE VI

β-CYCLOPENTYLETHYL ALKYL MALONIC ACIDS, $C_5H_9(CH_2)_2C(CO_2H)_2R$

R =	M. p., °C. (uncorr.)	Calcd., % C	Calcd., % H	Found, % C	Found, % H
H	126.5	59.96	8.06	59.97	8.07
C_2H_5	141–143	63.11	8.84	63.72	8.79
n-C_3H_7	137–138	64.42	9.16	64.43	9.21
n-C_4H_9	139–140.5	65.52	9.50	65.40	9.44
n-C_5H_{11}	124–127	66.62	9.70	66.04	9.64
n-C_6H_{13}	129.5–130	67.55	9.93	67.19	9.95

TABLE VII

CYCLOPENTYL ALKYL ACETIC ACIDS, $C_5H_9CH(CO_2H)R$

R =	B. p., °C.	M. p., °C. (uncorr.)	n_D^{20}		Calcd., % C	Calcd., % H	Found, % C	Found, % H
n-C_7H_{15}	155–160 (1.4 mm.)	....	1.4594	0.9312	74.27	11.58	74.39	11.64
n-C_8H_{17}	166–169 (2 mm.)	....	1.4609	.9279	74.93	11.75	74.63	11.67
n-C_9H_{19}	177–178.5 (1.4 mm.)	37–37.5	....	...	75.52	11.90	75.46	11.85
n-$C_{10}H_{21}$	189–190.5 (1.7 mm.)	34.5–36	....	...	76.05	12.02	76.08	12.03
n-$C_{11}H_{23}$	193–197 (1.3 mm.)	43.5–45.5	....	...	76.52	12.14	76.83	12.16

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[8] Y. Talvitie, Ann. *Acad. Sci. Fennicae*, **16**, 26A, 1 (1927).

[9] Wood and Scarf, *J. Soc. Chem. Ind.*, *42*, 13T (1923).

Undecyl Alcohol.[10]—From undecenyl alcohol by means of hydrogen and platinum-oxide platinum black in alcohol solution; b. p. 100–102° at 2 mm.

Undecyl Bromide.[6]—B. p. 134–137° at 18 mm.; n_D^{20}, 1.4571; d_4^{20}, 1.0521. Calcd. for $C_{11}H_{23}Br$: Br, 33.99. Found: 33.89.

TABLE VIII

β-CYCLOPENTYLETHYL ALKYL ACETIC ACIDS $C_5H_9(CH_2)_2CH(CO_2H)R$

R =	B. p., °C.	n_D^{20}	d_4^{20}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
H	115–118 (2.4 mm.)	1.4575	0.9849	69.18	10.33	69.01	10.30
C_2H_5	122–124.5 (1.3 mm.)	1.4590	.9602	71.68	10.95	71.71	10.90
n-C_3H_7	130–132 (1.9 mm.)	1.4595	.9533	72.66	11.19	72.22	11.08
n-C_4H_9	136–137 (1 mm.)	1.4608	.9435	73.52	11.40	73.34	11.38
n-C_5H_{11}	150–154 (1.9 mm.)	1.4610	.9360	74.27	11.58	74.03	11.57
n-C_6H_{13}	157–161 (1.9 mm.)	1.4616	.9303	74.93	11.75	74.93	11.64
n-C_7H_{15}	167–169 (2 mm.)	1.4621	.9252	75.52	11.90	75.57	11.88
n-C_8H_{17}	173–176 (1.5 mm.)	1.4629	.9210	76.05	12.02	75.80	11.94

The bacteriological work was carried out by W. M. Stanley. The same strain of bacillus was used as in previous papers in this series.

Summary

1. Two series of cyclopentyl acids have been prepared of the general formulas $C_5H_9CH(CO_2H)R$ when R varied from n-heptyl to n-undecyl and $C_5H_9(CH_2)_2CH(CO_2H)R$ when R varied from ethyl to n-octyl.
2. Bacteriological results showed those acids containing sixteen to eighteen carbon atoms were the most effective bactericides toward B. *Leprae.*
3. Comparisons of cyclopentyl and cyclohexyl substituted acids are given.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE SOLUBILITY OF META-NITRANILINE IN WATER

BY JAMES H. WALTON AND T. G. FINZEL

RECEIVED MARCH 27, 1928 PUBLISHED MAY 6, 1928

The following solubility determinations were made as a result of solubility studies carried out by Bateman and Baechler.[1] These investigators report a marked lack of agreement among the published solubility data[2] of this compound; further preliminary experiments made at the Forest Products Laboratory showed that saturated solutions are obtained with great difficulty.

[10] See Blaise and Guerin, *Bull. soc. chim.*, [3] 29, 1202 (1903).

[1] Bateman and Baechler, "The Solubility of some Amino and Nitro Derivatives of Benzene in Water at 25° C." Report from the Forest Products Laboratory, Madison, Wisconsin.

[2] Vaubel, J. *prakt. Chem.*, 52, 72 (1895); Carnelley and Thomson, J. Chem. *Soc.*, 53, 782 (1888).

Experimental

Materials.—The *m*-nitraniline melted at 112.5°. When recrystallized from methanol the melting point remained unchanged.

Method.—Six hundred cc. of boiled water was practically saturated at 15 to 20° above the temperature at which the solubility determination was made. The solution was cooled to the desired temperature and, after several hours, samples were removed. In sampling the saturated solution, muslin or filter paper did not remove the finely suspended solid phase from the solution. A miniature Gooch asbestos filter, as well as a Mandler filter of the type used in bacteriological work, proved satisfactory. This unusual difficulty in filtration is very evidently the cause of the lack of concordant results obtained by earlier investigators. Attention is further called to the extremely slow rate of solution of the m-nitraniline. In approaching saturation at 25°, without previous solution at a higher temperature, the solution was stirred for at least twenty-four hours before equilibrium was established. The solution was analyzed by two different methods.

1. The Titanium Trichloride Methods depends on the reduction of the nitro group by an excess of standard titanium trichloride in a hydrochloric acid solution, the reduction being carried out in a carbon dioxide atmosphere. The excess trichloride is titrated with a standard ferric alum solution, using ammonium sulfocyanate as an indicator. In using this method, it was found that below 35° a correction was necessary for the oxygen dissolved in the sample that was being analyzed.

2. The Sodium Nitrite Method[4] depends upon diazotizing the amino group of the m-nitraniline, using standard sodium nitrite and a starch–cadmium iodide solution as an outside indicator. In each of the above methods the value of the standard solution was established by means of

TABLE I

THE SOLUBILITY OF *m*-NITRANILINE IN WATER

Temp., °C.	Grams of m-nitraniline in 100 g. of solution $NaNO_2$ method	 $TiCl_3$ method
0	0.029	0.0302
10	.046	.0473
20	.072	.0732
25	..	.0914
35	.135	.1407
44	.211	.211
55	.309	.338
65.4	.523	.543
75	.815	.838
83.4	1.19	1.23

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[3] English, *J. Ind. Eng. Chem.*, 12, 994 (1920).

[4] Callan, Henderson and Stafford, *J. Soc. Chem. Ind.*, 39, 86T (1920).

pure m-nitraniline. The titanium trichloride method gave the more concordant results, making it especially applicable for small concentrations of m-nitraniline. The data obtained by this method are listed in the table.

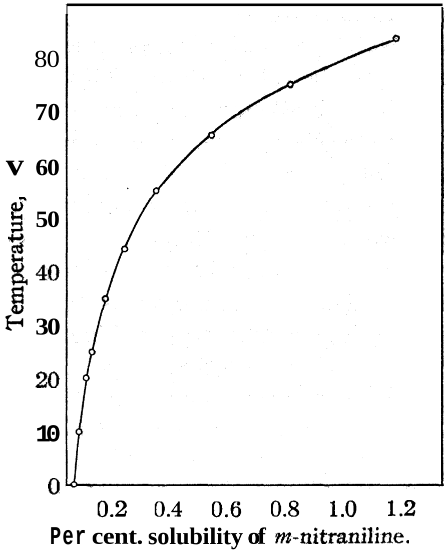

Fig. 1.

For the analysis of samples containing larger amounts of *m*-nitraniline, the nitrite method compares favorably with the titanium trichloride method, since in this case rather large volumes of the trichloride are necessary. To give some idea of the difference in the results, the sodium nitrite data are also given. When these results are plotted, a perfectly smooth curve results between the temperatures of 0 and 83.4". Attention is called to the fact that at the latter temperature Sidgwick and Rubie[5] obtained a solubility of 1.7%, while the average figures from the repeated determinations by the authors gave a value of 1.23%.

Summary

1. A study of the solubility of m-nitraniline in water has been made between the temperatures 0 and 83.4'.
2. In agitating m-nitraniline and water, it was shown that the solid phase settles with such difficulty and is so finely divided that either an asbestos or Mandler filter must be used as a sampler.
3. At 25° the rate of solution of m-nitraniline in water, near the saturation point, is extremely slow.
4. A comparison between the titanium trichloride method and the sodium nitrite method for the analysis of m-nitraniline has been made.

MADISON, WISCONSIN

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[5] Sidgwick and Rubie, J. Chem. *Soc.*, 119, 1013 (1921).

NEW BOOKS

Poems. BY "OPIFEX." The Chemical News, Ltd., Merton House, Salisbury Square London, E. C. 4, 1928. 105 pp. 12 X 19 cm. Price, 5 shillings.

We do not know who Opifex is, but in sending a copy for review he admits that he is a member of the American Chemical Society.

The initial four pages are given up to an amusing historical record in quatrains that tells what Democritus, John Dalton, Clerk Maxwell, Frankland, J. J. Thomson, Curie, Rutherford, Moseley, G. N. Lewis, Langmuir, Bohr and the Braggs did to the atom. The author had not got to Schroedinger and Heisenberg by the time he wrote it, There is a translation of verses read at a Weihnachts-kneipe at Zurich with Alfred Werner in the chair, in praise of chemistry; also a metrical protest against the misuse of the word chemist, a letter in verse to the editor and a Hymn to the author's Alma Mater. These take up sixteen pages that serve as preface to eighty-eight more pages of lyric appeal for religious faith. The author discusses in a single form of verse: "Intelligence," "Its Source," "Ignorance," "The Universe," "The Heavens," "The Earth," "Life," "Truth," "Mathematics," "Knowledge," "Light," "Smallness," "Man," "The Soul," "Ethics," "The Ancients," "Religion," "Sorrow," "Love," "Work," "Philosophy," "Unsolved," "Psychology" and "God."

A comprehensive list indeed. But most of it, somehow, sounds familiar. And the ringing lines that march with majesty into the memory, there to abide, have failed to register with the present reviewer.

E. H.

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. VIII. Nitrogen, Phosphorus. By J. W. MELLOR, D.Sc. Longmans, Green and Company, 55 Fifth Avenue, New York, 1928. x + 1110 pp. 156 figs. 25 X 16 cm. Price $20.00.

This volume is another monumental contribution. It is not only replete with references to the literature and with the most recent and detailed information about nitrogen and phosphorus, but it also maintains a just historical perspective regarding the contributions to our knowledge of these important elements. Moreover, it achieves the rare distinction of being an interesting and readable dictionary!

This latest volume will be welcomed eagerly by those who use the earlier volumes of this series, which now—having covered two-thirds of the elements—is approaching completion. It is dedicated by the Author, "To the Privates in the Great Army of Workers in Chemistry: their Names have been Forgotten; their Work Remains."

ARTHUR B. LAMB

Elementary Physical Chemistry, adapted from a Treatise on Physical Chemistry. By Hugh S. Taylor, D.Sc. (Liverpool), Professor of Physical Chemistry, Princeton University. D. Van Nostrand Company, Inc., Eight Warren Street, New York, 1927. ix + 531 pp. 108 figs. 14 × 22 cm. Price $3.75.

The purpose and scope of this text are best indicated in the words of the author: "The present volume attempts the presentation of material suitable for an introductory course in modern physical chemistry. It is adapted from the two volume 'Treatise of Physical Chemistry' which appeared under the author's editorship some three years ago. A need has been felt in several quarters for a single volume of a more elementary nature which should follow the general lines of development in the larger treatise, without, however, its details. This book is offered in response to such a demand."

The main topics and their arrangement are indicated by the chapter headings: The Atomic Concept of Matter; Energy in Chemical Systems; The States of Aggregation, I. The Gaseous State; II. The Liquid State; III. The Crystalline State; The Velocity and Mechanism of Gaseous Reactions; The Directions of Chemical Change; Solutions, Part I; Homogeneous Equilibria; Heterogeneous Equilibrium; Electrical Conductance and Ionization; Ionic Equilibrium, I. Weak Electrolytes; II. Strong Electrolytes; Photochemistry; Colloid Chemistry.

The book represents a notable departure from most texts which have appeared under a corresponding title. The changing emphases in physical chemistry are taken into account and certain traditional material has given place to topics of recent interest. This is particularly true of the presentation of chemical kinetics and the concepts fundamental to it, where the treatment is excellent, as might be expected from the eminent position of the author in this field.

The author relies upon present-day practice of teaching in courses in general chemistry much of the elementary physical chemistry that has generally occupied a considerable space in texts upon the latter subject. He, therefore, carries the student farther into the subject than would otherwise be possible. He assumes a knowledge of mathematics, including the calculus, saying, "Any teacher who would advise his students that he can attain to an understanding of the science as now developing without the mathematical knowledge required in the present volume is, in the opinion of the author, doing an ill service to his pupils." This attitude surely needs no defense. The day is past when a man can become a chemist with but a smattering of preparation in mathematics and physics.

It is to be regretted that the table of electronic structure of atoms given in Chapter I should be that of Bohr rather than the later arrangement of Main Smith and Stoner, which is given, but only for noble gases. It might be suggested, also, that the form of the periodic system given on page 10 should be changed to one corresponding better to atomic structure.

In the opinion of the reviewer, the sections dealing with thermodynamics are weaker than the rest of the book. Chapter VIII upon solutions could be improved. The treatment here is traditional rather than critical. Twelve pages are devoted to osmotic pressure, and the gas law for osmotic pressure is taken as defining an ideal solution. Molecular weight is calculated from vapor pressure lowering, not by the aid of Raoult's law but of a less accurate osmotic pressure relation. The third law of thermodynamics is sufficiently important to have a better treatment than that given in the chapter upon homogeneous equilibria.

The chapter upon heterogeneous equilibrium is particularly good, as is also the chapter upon photochemistry. This latter constitutes one of the few adequate presentations of this very important subject.

The book inevitably shows some traces of its origin as an abridgment of a larger work, but the net result of this is doubtless profit rather than loss. The reviewer takes pleasure in recommending it cordially to the attention of teachers of physical chemistry.

J. H. HILDEBRAND

Chemical Affinity. By L. J. HUDLESTON, Lecturer in Physical and Inorganic Chemistry at the University College of Wales, Aberystwyth. Monographs on Inorganic and Physical Chemistry, edited by ALEXANDER FINDLAY, D.Sc. Longmans, Green and Company, 55 Fifth Avenue, New York, 1928. vii + 138 pp. 5 figs. 15 × 22 cm. Price $2.75.

This book gives a comparatively brief and well written discussion of Thermodynamics with special reference to chemical reactions. The scope of the work may be indicated most conveniently by the chapter headings: Energy and its Transformations (First and Second Laws of Thermodynamics); Entropy; Free Energy; Solutions; The Nernst Heat Theorem and Third Law of Thermodynamics; Applications. Although it does not contribute anything new to the science or give a critical and comprehensive analysis of the evidence for the newer theories, it will be useful to students as an introduction to the more extensive treatises of Lewis and Randall or of MacDougall or to the works of Gibbs, and therefore deserves a place in every college library. The binding is poor.

GRINNELL JONES

Veroffentlichungen aus dem Kaiser-Wilhelm-Institut für Silikatforschung. (Publications from the Kaiser Wilhelm Institute for Silicate Research.) Edited by Dr. Wilhelm Eitel. Gebriider Borntraeger, W 35 Schoneberger Ufer 12 a, Berlin, 1928. vi + 262 pp. 55 figs. 19 × 26.5 cm. Price, unbound, 28 M.

This volume is the first of a series of collected publications of the Kaiser Wilhelm Institute for Silicate Research founded, in 1926, under the direction of Wilhelm Eitel. The twenty articles which it contains have all been previously published elsewhere, for the most part in the *Zeitschrift für Kristallographie* and in the *Zeitschrift fur anorganische* und *allgemeine Chemie.* The articles have not, strictly speaking, been reprinted here but are simply separates furnished by the original publishers and bound together in the present volume.

Most of the articles are concerned with the crystallographic analysis by means of x-rays of various minerals and of a few organic substances, but the longest article (84 pages) and the one of the most general interest is by E. Herlinger and is entitled "Concerning the Newer Developments of Geochemistry." This article reviews in a thorough fashion the recent work on the elementary composition of the earth and on the chemical transformations which have taken place both in the interior parts of the earth and in its crust.

The volume should constitute a useful collection for mineralogists, chemists and geologists interested in the chemistry and physics of the silicates. It is dedicated to "Adolf von Harnack, the Tireless Promoter of Research."

ARTHUR B. LAMB

Handbuch der biologischen Arbeitsmethoden. (Handbook of Biochemical Methods.) Edited by Professor Dr. EMIL ABDERHALDEN, Director of the Physiological Institute of the University of Halle an der Saale. Abt. III, Physikalisch-chemische Methoden, Teil B, Heft 4. Urban and Schwarzenberg, Friedrichstrasse 105, Berlin N 24, Germany, 1927. 120 pp. 60 figs. 18 × 25.5 cm. Price, M 7.

The book comprises three articles on recent developments in methods of colloid research, as applied to biological chemistry. The first on "Electrodialysis" by Mona Spiegel-Adolf discusses with some detail the methods and apparatus used by recent investigators. Ten pages are devoted to an enumeration of applications of electrodialysis, during the last five years. Many of these are quite outside the field of biology. The article by Arne Tiselius on "Methods of Determining the Mobility and Charge of Colloid Particles," describes especially methods developed and used at Upsala for measuring the mobility of protein solutions by the moving boundary method. The article includes a good discussion of the theory of cataphoresis, and of the precautions which are necessary in order to get reliable measurements of mobility. The final article by Svedberg on "Molecular Weight Determinations of Proteins by Centrifugation" summarizes his brilliant researches in this field. It includes a development of the theory and fundamental equations for the method, a description of the apparatus as developed, with numerous illustrations, and the results obtained with hemoglobin and egg albumin. The conclusive way in which the method has shown that hemoglobin solutions contain only particles of molecular weight 66,800 illustrates what'a help it will be in the study of other proteins.

NORMAN D. SCOTT

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[CONTRIBUTION PROM THE CHEMICAL ENGINEERING DEPARTMENT, THE OHIO STATE UNIVERSITY]

ZIRCONIUM SULFATE AS A REAGENT FOR THE DETECTION OF POTASSIUM[1]

BY RUFUS D. REED AND JAMES R. WITHROW

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Work under way in this Laboratory indicated the possibility of using zirconium sulfate as an alternative test for the detection of potassium. Potassium sulfate has long been known as a reagent for the precipitation of zirconium.[2] No one appears to have taken the trouble to find how sensitive zirconium sulfate itself would be in the detection of potassium. Therefore the sensitiveness of a zirconium sulfate solution for potassium was investigated.

Experimental

To investigate the sensitiveness of zirconium sulfate solution as a qualitative test for potassium it was necessary to prepare the following reagents and to determine their purity.

Zirconium Sulfate Solution.—This solution was prepared by stirring powdered zirconium sulfate with distilled water for four hours. The solution was allowed to stand overnight at room temperature. It was filtered and analyzed to determine purity to preclude interfering substances. It contained no cerium earth metals, cobalt or tartrate. Quantitative analysis for zirconium by the Lundell and Knowles method[3] showed 0.2096 g. of zirconium sulfate per cc. of solution. This solution was prepared at 28°. It would deposit crystals on standing overnight but these could be dissolved by warming the bottle of solution in hot water for a few minutes.

Potassium Sulfate Solution.—A saturated potassium sulfate solution containing 0.0545 g. of elemental potassium per cc. was prepared. To preclude possible interfering substances, this solution was analyzed qualitatively and found free from hydroxyl, carbonate, sulfide, thiosulfate, phosphate, sodium and ammonium ions. Dilution of portions of this stock solution gave the more dilute solutions used.

Sodium Sulfate Solution.—To determine the effect of the sodium ion on the detection of potassium by zirconium sulfate, a saturated solution of potassium free sodium

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[1] Read before Detroit meeting, September. 1927.

[2] Fresenius, "Qualitative Chemical Analysis," C. A. Mitchell's translation of 17th edition, John Wiley and Sons, Inc., New York, 1921, p. 182; Venable, "Zirconium and Its Compounds," Chemical Catalog Co., New York, 1922, pp. 81–84.

[3] Lundell and Knowles, THIS JOURNAL, 41, 1801 (1919).

sulfate was prepared. Mixing of this solution with the potassium sulfate solution gave the mixtures of sodium and potassium sulfates used.

Sodium Cobaltic Nitrite Solution.—For comparison of sensitiveness of sodium cobaltic nitrite and zirconium sulfate for the detection of potassium, a solution of sodium cobaltic nitrite was prepared according to the method of Scott.[4]

General Procedure for Potassium Detection.—In all the series of experiments in which potassium was tested for by zirconium sulfate, exactly 1cc. portions of potassium sulfate solutions of varying concentrations were pipetted into dry test-tubes. Exactly 1cc. portions of zirconium sulfate solution were added. The mixtures after shaking were allowed to stand at room temperature for one hour. Then the tubes were immersed in ice water until a reaction was noticed. At the start of the run, the walls of the tubes were well rubbed with a glass rod to promote

Table I

Sensitiveness of Zirconium Sulfate Solution as a Test for Potassium

Total volume, 2 cc. Zirconium sulfate, **0.2096** g. per test

Expt.	K, g. per sample	Results at room temperature	Results on cooling to 0°C.
1	0.05455	Precipitate at once	...
2	.02728	Precipitate at once	...
3	.01818	Cloudy at once	...
4	.01362	Precipitate in one-half hour	...
		Precipitate in one-half hour	
5	.00909	Slight precipitate in one-half hour	...
6	.00495	Cloudy in one hour	More cloudy in one-half hour, precipitate in one hour
7	.00260	None one hour	Cloudy in one-half hour, precipitate in one hour
8	.00176	None one hour	Cloudy in one hour, precipitate in one and one-half hours
9	.00107	None one hour	Cloudy one and one-half hours, precipitate in 2 hours
10	.00072	None one hour	Slightly cloudy in one and one-half hours, more so in two hours, precipitate in 2 and one-half hours
11	.00053	None one hour	Slightly cloudy in one and one-half hours, more so in 2 hours, precipitate in two and one-half hours
12	.00030	None one hour	Slight precipitate in one hour
13	.00007	None one hour	Slightly cloudy in two hours
14	.00000	None one hour	Slightly cloudy in two hours, precipitate in two and one-half hours
15	.00000	None one hour	Clear in two and one-half hours
16	.00000	None one hour	Slight precipitate in four hours

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[4] Scott, "Qualitative Chemical Analysis," 4th edition, 2d printing, D. Van Nostrand Co., New York City, 1923, p. **330.**

crystallization. This rubbing was repeated at half-hour intervals throughout the run.

Sensitiveness of Zirconium Sulfate Solution as a Test for Potassium.—To determine the sensitiveness of zirconium sulfate for potassium when no possible interfering ions were present, a series of experiments was made, varying the amount of potassium and keeping all other factors constant. The results are given in Table I.

Discussion.—On cooling in ice water the deposit formed in Expt. 11 containing 0.00053 g. of potassium (0.0068 molal potassium sulfate or 0.05% elemental potassium) was slightly more than in Expt. 14 containing no potassium. The deposit in Expt. 12 containing 0.3 mg. of potassium although formed after one hour's cooling did not increase in magnitude on standing. This deposit and the deposit in Expt. 13 containing 0.07 mg. of potassium were of about the same magnitude as the deposit in the blank Expt. 14. The formation of deposits in the two blanks, Expts. 14 and 16, emphasized the need of running concurrently a blank in tests for traces of potassium with zirconium sulfate.

The appearance of the precipitate varied. If it came at once on adding the reagent or after rubbing the walls of the tube with a stirring rod, it appeared to be amorphous. If it formed slowly with no agitation, it was needle shaped and collected in fan-like bundles.

An idea of the amount of potassium present in a solution could be gained from the time required for the appearance of a deposit. If 18.2 mg. of potassium was present in 2 cc. of mixture, a deposit or cloudiness was formed at once. Those solutions containing less than 18.2 mg. of potassium and more than 4.95 mg. of potassium gave a precipitate or cloudiness within an hour at room temperature. Those solutions containing 0.5 mg. to 2.6 mg. of potassium per cubic centimeter gave a precipitate only after cooling in ice water for from one to two and one-half hours depending upon the amount of potassium present.

Comparison of Sensitiveness of Zirconium Sulfate Solution for Potassium with that of Sodium Cobaltic Nitrite Test for Potassium.—To compare the sensitiveness of these two reagents, a series of tests for potassium with sodium cobaltic nitrite was made. The method of testing with sodium cobaltic nitrite was that of Scott.[5] A comparison with a blank was made where there was any doubt as to turbidity or deposit. The results appear in Table II.

Discussion.—Consideration of the time factor showed that: (1) both sodium cobaltic nitrite and zirconium sulfate gave immediate tests for potassium when 18.15 mg. of potassium was present. (2) With lower concentrations of potassium, the sodium cobaltic nitrite solution is a quicker test for potassium than zirconium sulfate solution. The presence

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[5] Ref. 4, p. 151.

TABLE II

COMPARISON OF SENSITIVENESS OF SODIUM COBALTIC NITRITE TEST AND OF ZIRCONIUM SULFATE TEST FOR POTASSIUM.

Total volume, 2 cc.

Expt.	K, g. per sample	Time for reaction with sodium cobaltic nitrite	Time for reaction with zirconium sulfate. Cooling to 0°C.
1	0.01818	Immediate precipitate	Immediate cloudiness at room temperature. No cooling
2	.00107	Slight precipitate in five minutes	Cloudy in one and one-half hours, cooling; precipitate in two hours, cooling
3	.00072	Slight precipitate in five minutes	Cloudy in two hours, cooling; precipitate in two and one-half hours
4	.00053	Slightly turbid in five minutes, slight precipitate in ten minutes	Precipitate in two hours, cooling
5	.00030	Slightly turbid in fifteen minutes, slight precipitate in one hour	Slight precipitate in one hour, no increase on standing. Same bulk of precipitate as blank at end
6	.00014	Slightly turbid in one hour, slight precipitate in two and one-half hours	No more test than blank
7	.00010	Very slight precipitate in five hours	No experiment run
8	.00007	Slight precipitate in twenty-three hours	No more test than blank
9	.00005	Clear, twenty-three hours	No experiment run
10	.00000	Clear, twenty-three hours	Slightly cloudy in two hours, precipitate in two and one-half hours

of 0.53 mg. to 0.3 mg. of potassium can be detected with sodium cobaltic nitrite within five to fifteen minutes, while it required one hour at room temperature and two hours' cooling to 0° to detect 0.5 mg. of potassium with zirconium sulfate solution.

As the sodium cobaltic nitrite test is usually applied according to directions of Scott[5] the absence of a precipitate with sodium cobaltic nitrite after ten to twenty minutes is considered as satisfactory proof of the absence of potassium. This work showed that as ordinarily applied the sodium cobaltic nitrite test is a little more delicate for potassium than zirconium sulfate when used for the longer time which we find desirable. Allowing the sodium cobaltic nitrite test, however, to stand for a longer time than is customary and comparing to a blank test, the sensitiveness of sodium cobaltic nitrite for potassium is 0.07 mg. of potassium as compared to 0.53 mg. of potassium with zirconium sulfate solution.[6]

[6] Bray, THIS JOURNAL, 31, 611 (1909), obtained with the sodium cobaltic nitrite test a turbidity within one to four minutes with 0.3 mg. of potassium, while we did not secure therewith a slight turbidity until fifteen minutes and a slight precipitate in one

Effect of Sodium Ion on the Detection of Potassium by Zirconium Sulfate Solution.—In qualitative analysis potassium ions are generally associated with sodium ions, ammonium ions and various anions. While the ammonium ions and interfering anions can be removed by evaporation with hydrochloric or sulfuric acid and gentle ignition, the sodium ion remains. Therefore it is necessary to determine the extent to which the sodium ion interferes with the detection of potassium by zirconium sulfate solution. The results of this work are given in Table III.

TABLE III

THE EFFECT OF SODIUM ION UPON THE DETECTION OP POTASSIUM BY ZIRCONIUM SULFATE SOLUTION

Total volume, 2 cc. Zirconium sulfate per test, 0.2096 g.

Expt.	K, g. per sample	Na, g. per sample	Na/K	Results at room temperature	Results on cooling to 0°C.
1	0.03632	0.0266	0.7324	Precipitate at once	...
2	.02728	.0399	1.4646	Precipitate, few minutes	...
3	.01816	.0532	2.929	Precipitate, one hour	Increased
4	.01362	.0598	4.394	Precipitate, one hour	Increased
5	.00909	.0665	7.317	None, one hour	Precipitate, one-half hour
6	.00495	.0725	14.65	None, one hour	Precipitate, one hour
7	.00304	.0748	24.58	None, one hour	Precipitate, one hour
8	.00260	.0760	29.26	None, one hour	Precipitate, one hour
9	.00210	.0767	36.19	None, one hour	Small precipitate, one hour
10	.00000	.07441	....	None, one hour	Opalescence, four hours
11	.00000	.0000	....	None, one hour	Precipitate, four hours
12	.00176	.07201	41.9	None, one hour	Precipitate, one hour
13	.00107	.07295	68.0	None, one hour	Precipitate, two and one-half hours
14	.00072	.07343	102.4	None, one hour	Precipitate, two and one-half hours
15	.00053	.07368	139.0	None, one hour	Precipitate, one and one-half hours
16	.00030	.07401	246.7	None, one hour	Precipitate, one and one-half hours
17	.00007	.07432	1061.0	None, one hour	None, two and one-half hours
18	.00000	.07441	....	None, one hour	Cloudy, one and one-half hours; precipitate, 'two hours

Discussion.—This work indicated that in the presence of very concentrated sodium sulfate solution, zirconium sulfate solution would detect

hour; but our results showed that by allowing the sodium cobalticnitrite test to stand for one day, a test for 0.07 mg. of potassium would be secured while Bray did not push his test farther than 0.1 mg. of potassium, for which he obtained a precipitate in six to ten hours. We secured a test for this amount of potassium in five hours. Bray used a total volume of 10 cc., while we used a total volume of 2 cc., obtaining more sensitive results.

1.76 mg. of potassium in 2 cc. of mixture. Expt. **18,** a blank, indicated that cooling for so long a time as two hours might cause a deposit to form when no potassium had been added, thus prohibiting prolonged cooling.

Comparison of the work in Table III with that in Table I indicated that: (1) the presence of sodium sulfate lowered the sensitiveness of zirconium sulfate for potassium from **0.53** mg. to 1.76 mg. (2) When potassium was present to the extent of 9 mg. or more, the presence of sodium retarded the test for potassium with zirconium sulfate about half an hour—it doubled the time. When potassium was present in amounts less than 9 mg. and 1.76 mg. or more, there was little or no difference in the time required for detection of potassium with zirconium sulfate. For amounts of potassium below 1.76 mg., the presence of sodium did not affect the time required for detection of potassium, but caused a deposit to form when no potassium had been added. As in the corresponding Experiment 12, Table I, in which no sodium was present, Expt. **16** containing **0.3** mg. of potassium gave a deposit with zirconium sulfate sooner than some of the more concentrated solutions of potassium. The amount of the deposit was of the same magnitude as that of the blank, indicating the need of a blank for comparison at low potassium concentrations.

Influence of Concentration of Zirconium Sulfate Solution on Detection **of** Potassium Both in the Presence and Absence of Sodium.—The stock solution was diluted to one-half strength in an attempt to eliminate precipitation in the blank. A dilute solution of the reagent would not crys-

TABLE IV

INFLUENCE OF CONCENTRATION OF ZIRCONIUM SULFATE SOLUTION UPON TEST FOR POTASSIUM BOTH IN THE PRESENCE AND ABSENCE OF SODIUM

Total volume, 2 cc. Zirconium sulfate, 0.1048 g.

Expt.	K, g. per sample	Na, g. per sample	Na/K	Results in one hour, room temp.	Results on cooling to 0°C.
1	0 00000	....	...	Opalescence	No change, four and one-half hours
2	...	0.07441	...	Opalescence	No change, four and one-half hours
3	...	,03720	...	Opalescence	No change, four and one-half hours
4	.0026	.07485	29.26	Cloudy	Small precipitate, one hour
5	.0026	....	...	None	Small precipitate, one hour
6	.00176	.07201	41 9	None	Opalescent, one hour; precipitate, one and one-half hours
7	.00176	....	...	None	Opalescent, one and one-half hours; precipitate, two hours
8	.00072	.07343	102.4	Opalescent	Cloudy, two and one-half hours; precipitate, four and one-half hours
9	.00072	....	...	Opalescent	Increased, three hours; no precipitate, four and one-half hours
10	.0003	....	...	None	Opalescent, one hour; no change, four and one-half hours
11	.0003	.07401	246.7	None	Opalescent, one hour; no change, four and one-half hours

tallize out on standing and so the warming up, mentioned in the section on preparation of zirconium sulfate, would be avoided. The results appear in Table IV.

Discussion.—In all experiments containing sodium sulfate except the blank 3, a deposit of apparently hydrated sodium sulfate formed on cooling to 0°. This would be dissolved on warming to room temperature for a few minutes. Any potassium zirconyl sulfate which might be present was undissolved.

The degrees of opalescence in the blanks 1, 2, 3 and in 10 and 11 containing 0.3 mg. of potassium were the same. This indicated that 0.3 mg. of potassium could not be detected by 10.48% zirconium sulfate. Expt. 9, containing 0.72 mg. of potassium, gave more opalescence after three hours' cooling than the blanks.

Comparing the results given above with the corresponding results in Table I and III where the concentrated zirconium sulfate was used showed: (1) in the absence of sodium, 20.96% zirconium sulfate solution detected 0.5 mg. of potassium while 10.48% zirconium sulfate solution detected 0.7 mg. of potassium. Either solution failed to detect the presence of 0.3 mg. of potassium in 2 cc. of mixture. Dilution of the reagent did not lower the sensitiveness of zirconium sulfate for potassium, but in the presence of sodium the dilution of the zirconium sulfate increased its sensitivity for potassium from 1.76 mg. to 0.7 mg. This increase in sensitivity was due to the non-formation of a deposit in the blank which occurred when the concentrated zirconium sulfate was used. (2) In the absence of sodium, the time required for the detection of potassium by zirconium sulfate was increased about one-half hour in all experiments. In the presence of sodium, the dilution of reagent increased the time required to detect potassium half an hour in the case of 1.76 mg. of potassium only.

The absence of a misleading deposit in the blank removed the serious objection that it was not a sure test for small amounts of potassium and increased the sensitivity of the test when sodium was present.

Summary of Conclusions

1. A concentrated zirconium sulfate solution detected 0.00053 g. of potassium (0.0068 molal potassium sulfate, 0.05% elemental potassium or 0.5 mg. of potassium) or more, when no sodium was present. It detected 1.76 mg. of potassium when sodium was present.

2. Large amounts of sodium sulfate retarded the detection of potassium in concentrated solutions but had little or no effect when the amount of potassium was small.

3. Zirconium sulfate when applied for the longer time we found necessary is almost as delicate a test for potassium as is sodium cobaltic nitrite when the latter is applied in the usual way. If the latter test is allowed to

run for a longer time than is customary, it can be made more sensitive for potassium than zirconium sulfate solution.

4. With dilute solutions of potassium sulfate—0.5 mg. of potassium—a comparison blank test with water and zirconium sulfate was needed. When sodium was present, a blank using sodium sulfate and zirconium sulfate was used for comparison with the solution tested.

5. Dilution of the zirconium sulfate solution to 10.48%, or one-half strength, had little or no effect upon its sensitiveness for potassium in the absence of sodium and increased the sensitiveness for potassium from 1.76 mg. of potassium to 0.7 mg. of potassium in the presence of sodium. No deposit in the blank test was formed.

6. To detect potassium with zirconium sulfate, add to the solution to be tested an equal volume of zirconium sulfate solution. If a deposit does not form at room temperature, cool in ice water. With small amounts of potassium a comparison with a blank is necessary.

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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN LABORATORY OF THE UNITED STATES BUREAU OF CHEMISTRY AND SOILS]

THE FREE ENERGY AND FUGACITY IN GASEOUS MIXTURES OF HYDROGEN AND NITROGEN

BY ALBERT R. MERZ AND COLIN W. WHITTAKER

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Knowledge concerning the free energies and fugacities of gases in mixtures is very meager. Lewis and Randall[1] assumed, *in the absence of theoretical or experimental investigations on the subject,* that every gaseous solution is a perfect solution and therefore that at a given temperature and total pressure the fugacity of each constituent is proportional to its mole fraction or to its partial pressure. This assumption was based on the supposition "that the solution of a given pair of substances will be more nearly perfect when the density of the solution is less" and by reason of the fact that "even among liquids numerous cases occur where there is a close approach to the perfect solution."

Lurie and Gillespie,[2] applying this rule to the calculation of the equilibrium pressures of ammonia, in mixture with nitrogen, over $BaCl_2 + BaCl_2 \cdot 8NH_3$, found in the region where it could be applied that it gave results in fair agreement with the observed equilibrium pressures. This region, however, was limited to pressures of less than 17 atmospheres.

Gibson and Sosnick,[3] using the experimental results of Masson and

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

[2] Lurie and Gillespie, THIS JOURNAL, 49, 1154 (1927).

[3] Gibson and Sosnick, *ibid.*, 49, 2172 (1927).

Dolley,[4] have recently calculated the fugacities and free energies of ethylene and argon in their mixtures up to pressures of 125 atmospheres. The rule of Lewis and Randall was found to be closely obeyed at low pressures. At about 50 atmospheres it was in error by 0 to 20%, according to the mole fraction, while for argon at zero concentration and about 100 atmospheres the fugacity is nearly twice the value calculated on the assumption of a perfect solution.

The experimental results of Bartlett[5] make possible the calculation of the fugacities of hydrogen and nitrogen in mixtures at 0° and under pressures ranging up to 1000 atmospheres. A full description of the method of calculation of fugacities from the isotherms of binary mixtures has already been given by Gibson and Sosnick[3] and need not be repeated here. Bartlett reports his values in terms of "density D," expressed in grams per liter. Division of the density D_p at pressure P of a given mixture by density, D_1, of the same mixture at 1 atmosphere, gives the volume of gas at 1 atmosphere compressed to 1 liter at P atmospheres. We assume, as did Bartlett, that at 1 atmosphere the sum of the separate volumes equals the volume of the mixture. The result of the division, therefore, also gives the "density D" of Masson and Dolley. The mole fraction was calculated from the volume per cent., V.P., by first obtaining the molal volumes v_1 and v_2 of hydrogen and nitrogen, respectively, from the liter weight L of these gases, namely, $L_{H_2} = 0.898$ g. per liter at 0° and 1 atm. and $L_{N_2} = 1.2507$ g. per liter at 0° and 1 atm., and then employing the equation

$$N_1 = 1 - N_2 = (V.P.)_1/v_1 \; \frac{(V.P.)_1}{v_1} + \frac{100 - (V.P.)_1}{v_2} \qquad (1)$$

The molal volumes, v, of the mixture as obtained from the equation

$$v = \frac{N_1v_1 + N_2v_2}{D_p/D_1} \qquad (2)$$

are given in Table I.

TABLE I

MOLAL VOLUMES OR MIXTURES OF HYDROGEN AND NITROGEN

P (atmos.)	Mole Fractions of N_2									
	0.0000	0.1152	0.2464	0.4495	0.5415	0.6595	0.7404	0.8633	0.9391	1.000
1	22449.9	22444.2	22437.6	22427.7	22423 1	22417 2	22413.2	22407.1	22403.3	22400.3
50	464.1	463.2	460.9	457.5	456.3	452.9	450 6	446.3	443.8	441.1
100	239.4	238.4	2374	234.6	2332	230.5	228.6	225.0	222.9	220.5
200	127.8	126.8	126.6	125.2	123.9	122.5	1210	119.0	117.7	116.4
300	90.5	90.3	90.0	89.6	88.7	878	873	86.2	85.6	85.0
400	72.0	72.1	72.3	72.3	72.0	71.5	71 3	70.9	70.8	70.5
600	63.4	53.9	54.6	55.4	55.5	55.9	56.1	55.7	56.9	56.9
800	44.1	44.8	45.8	47.1	47.4	48.2	48.7	49.5	49.9	50.5
1000	38.5	39.4	40.5	42.1	42.7	43.5	441	45.2	458	46.4

The partial molal volumes, calculated by means of Sosnick's[6] equation, are contained in Table II.

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[4] Masson *and Dolley, Proc. Roy. Soc. (London),* 103A, *524 (1923).*

[5] *Bartlett,* THIS JOURNAL, 49, *1955 (1927).*

[6] Sosnick, *ibid.,* 49, *2256 (1927).*

Table II

Partial Molal Volumes or Hydrogen and Nitrogen in Their Mixtures

	Mole Fractions of N_2											
	0.0		0.2		0.4		0.6		0.8		1.0	
P (atmos.)	V_1	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	$\bar{V}_2$	$\bar{V}_1$	V_2
1	22449.9	...	...	...	...	...	...	...	...	...	...	22400.3
50	464.1	457.1	465.0	451.0	466.4	447.5	468.9	444.6	475.5	441.9	481.6	441.1
100	239.4	236.6	239.9	229.9	241.3	226.7	243.9	224.1	249.4	221.6	253.6	220.6
200	127.8	124.2	128.1	122.7	129.1	120.3	131.4	118.0	113.6	116.7	136.4	116.4
300	90.5	88.6	90.6	88.0	91.1	86.9	92.1	85.9	93.5	85.3	94.9	85.0
400	72.0	73.9	72.1	72.8	72.5	71.8	73.1	71.2	73.9	70.7	74.8	70.5
600	53.4	59.2	53.6	57.7	53.6	57.3	53.8	57.3	54.2	57.0	54.6	57.0
800	44.1	50.0	44.0	50.3	43.9	50.6	44.0	50.6	44.1	50.5	44.0	50.5
1000	38.5	45.9	38.5	46.0	38.3	46.4	38.5	46.4	38.4	46.4	38.5	46.4

The values of $\alpha = RT/P - \bar{v}$ were calculated from Table II and plotted against P for various mole fractions. Graphical integration of these curves gave the values of $\int_0^P \alpha\, dP$ and by use of the equation

$$\log f/\text{N}P = \frac{1}{2.3026 \times 82.07 \times 273.1} \int_0^P \alpha\, dP$$

the values of $f/\text{N}P$ and of $\log f$ were obtained.

The free energies given in Table III were obtained by multiplying these values of $\log f$ by **1250.45 = 2.3026 RT, R** here being expressed in calories per degree.

Table: III

Free Energy or Hydrogen and Nitrogen

	$\text{N}N_2$											
	0.0		0.2		0.4		0.6		0.8		1.0	
P (atmos.)	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2
1	1		−120	−881	−276	−498	−497	−278	−873	−122		0
50	2155		2035	1243	1880	1619	1662	1837	1289	1992		2112
100	2551		2432	1623	2278	1997	2062	2210	1697	2363		2483
200	2966		2846	2020	2696	2387	2482	2595	2128	2744		2861
300	3223		3104	2271	2957	2632	2745	2836	2397	2983		3099
400	3418		3299	2465	3154	2823	2943	3025	2597	3171		3283
600	3714		3597	2776	3454	3129	3245	3330	2901	3474		3587
800	3948		3831	3035	3689	3388	3480	3589	3137	3732		3844
1000	4146		4029	3268	3887	3622	3677	3823	3336	3967		4079

Table IV

Deviation of Hydrogen and Nitrogen in their Mixtures from the Perfect Gas Law $f/\text{N}P = 1$

	$\text{N}N_2$											
	0.0		0.2		0.4		0.6		0.8		1.0	
P (atmos.)	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2
1	1.002	0.999	1.002	0.999	1.002	0.999	1.002	0.999	1.002	0.999	1.002	0.999
50	1.058	.997	1.060	.987	1.063	.986	1.066	.981	1.074	.979	1.078	.978
100	1.096	1.020	1.101	.993	1.105	.989	1.113	.976	1.137	.969	1.153	.965
200	1.176	1.081	1.179	1.031	1.193	1.013	1.208	.990	1.258	.977	1.297	.971
300	1.261	1.152	1.266	1.091	1.285	1.061	1.307	1.031	1.375	1.011	1.426	1.002
400	1.353	1.241	1.358	1.170	1.384	1.131	1.412	1.093	1.493	1.073	1.555	1.055
600	1.556	1.476	1.568	1.383	1.605	1.325	1.638	1.278	1.739	1.250	1.863	1.231
800	1.796	1.796	1.808	1.672	1.855	1.600	1.895	1.546	2.015	1.508	2.159	1.485
1000	2.069	2.205	2.086	2.052	2.141	1.969	2.185	1.902	2.325	1.858	2.489	1.828

The ratios of f/NP are given in Table IV. These values show the deviations from the perfect gas law $f = NP$ of hydrogen and nitrogen, respectively, in their mixtures.

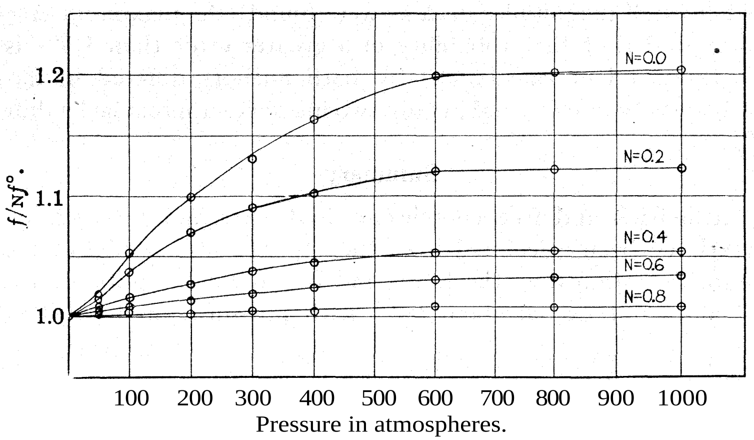

Fig. 1.—Deviation of hydrogen in hydrogen-nitrogen mixtures from the law of the perfect solution $f/Nf^\circ = 1$.

The ratios of f/Nf° for hydrogen are plotted in Fig. 1 against pressures for the different mole fractions and similarly for nitrogen in Fig. 2. It will be observed from these graphs that even at pressures around 1000 atmospheres the deviation from the law of the perfect solution $f/Nf^\circ = 1$ is only about 20%. It is particularly noteworthy that near the limiting case for hydrogen at zero concentration and 1000 atmospheres the density of the solution is about six-tenths that of water.

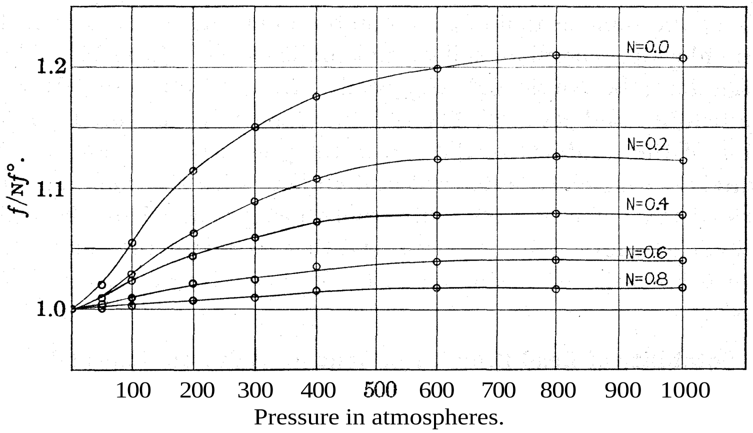

Fig. 2.—Deviation of nitrogen in hydrogen-nitrogen mixtures from the law of the perfect solution $f/Nf^\circ = 1$.

The accuracy of the calculation of the fugacities is dependent primarily upon the determination of the slopes of the curves of A against N. These slopes in turn are dependent upon the magnitudes of A. With such small magnitudes of A as were found (the maximum $A = 4.6$) it is estimated that the probability of a greater error than 1.5% is very slight. Independent calculations by both authors differed in most instances by less than 0.3% and in only two instances approached a difference of 1.5%.

Summary

The fugacities and free energies of hydrogen and nitrogen in their mixtures have been calculated from the experimental results of Bartlett. Maximum deviation from the Lewis and Randall assumption of a perfect solution does not exceed about 20% with pressures up to 1000 atmospheres.

WASHINGTON, D. C.

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

THE SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AND THE CALCULATION OF THE ACTIVITY COEFFICIENT FROM SOLUBILITY MEASUREMENTS[1]

BY MERLE RANDALL AND WILLIAM V. A. VIETTI

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Lewis and Randall[2] found that the activity coefficient of lead bromide was about the same as that of cadmium bromide, and was less than that of barium chloride, potassium sulfate and similar salts. Lead bromide must not, therefore, be considered a typically strong electrolyte. It is moderately soluble and its solubility can be accurately measured. A determination of the solubility of this salt in the presence of several strong and moderately strong electrolytes was undertaken, with the hope that the deviations of the activity coefficients from those predicted by the principle of the ionic strength would be large, and that we might thus find a further experimental basis for prediction as to the behavior of mixtures of electrolytes.

Solubility of Lead Bromide in Aqueous Salt Solutions at 25°

Lead bromide was prepared from dilute solutions of recrystallized lead nitrate and sodium bromide by metathesis. The salt was purified by recrystallization and was

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[1] Presented at the Joint Session of California Section of the American Chemical Society and the Pacific Division of the American Association for the Advancement of Science at Stanford University, California, June 26. 1924. Referred to by Randall, *Trans. Faraday Soc.*, 23, 502 (1927).

[2] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 424.

considered pure when successive determinations of the solubility gave constant values. The added salts were ordinary chemically pure materials purified by recrystallization. The solvent solutions were made up by weight. All compositions are expressed as moles per 1000 g. of water, vacuum corrections being employed. So-called conductivity water was used.

Sufficient lead bromide, so that about 25 g. of the solid phase would remain after equilibrium was established, was placed in a long-necked flask (250-cc. Pyrex distilling flask body) and washed several times with water or the solution to be used as a solvent. About 200 cc. of the solvent solution was then added and the flask sealed by drawing off the neck near its end, Equilibrium was approached from undersaturation and supersaturation in each case.

The flasks were fastened to a rotating shaft (about 30 r.p.m.) suspended in a water thermostat maintained at 25 + 0.01°. With the neck of the flask at an angle, the solid filled the neck at one phase of the rotation and was replaced by the residual air at another. Lead bromide is slowly soluble in the higher concentrations of added salt and the method of shaking here described proved to be quite efficient.

After the period of rotation shown in Col. 3 of Table I, the flask was removed from the rotator and placed in a rack in the thermostat. The tip of the flask was then broken and the solution filtered by blowing it out at the rate of about 5 cc. per minute through a tube whose lower end was submerged in the solution and was lightly plugged with absorbent cotton, the first 25 cc. being discarded. Weighed portions were then taken for analysis.

For the determination of bromide a slight excess of a known silver nitrate solution was added (weight buret); the solution was heated to coagulate the silver bromide, allowed to cool and acidified with a small amount of nitric acid. The slight excess of silver was estimated by volumetric titration (Volhard) with a very dilute solution of potassium thiocyanate.

Lead was determined as lead peroxide. Bromide was removed as bromine by successive evaporations with nitric acid, the nitrates were dissolved in water and the solution acidified by the addition of 10 cc. of nitric acid (sp. gr., 1.42) per 100 cc. of solution. This solution was electrolyzed (four to eight hours) at 6 volts between a platinum disk cathode and a 300cc. platinum dish as anode. In order to secure an adherent deposit, the surface of the dish was sand-blasted. The deposit was washed free of soluble salts in *situ* before opening the circuit, then with water and three successive portions of absolute alcohol. The deposit was dried at 180–200° in an electric oven for two hours, cooled and weighed. The resulting peroxide varied from a rich brown-red to black, the color varying according to the thickness of the deposit.

The composition of the solid phase in equilibrium with the solutions was determined by direct analysis for lead and bromine as above. Weighed moist samples were taken, dried to constant weight at 110° and then analyzed. Corrections were made for the amount of solution in contact with the solid phase and the composition was calculated for dry solid phase.

The solubility of lead bromide in water, as determined directly by evaporation of the solution, was 0.02674 mole per 1000 g. of water; as calculated from the bromide by comparison with silver solution, 0.02683; and as calculated from the lead weighed as lead peroxide, 0.02684 mole per 1000 g. of water.

The molality of the added salt is shown in the first column of Table I. The second column shows the molality of the lead bromide in the ordinary sense, that is, as calculated from the molality of the ion not present as a constituent of the solvent solution, the third the time of rotation, the fourth the logarithm of the mean molality of the lead and bromide ions and the last the square root of the ionic strength.

TABLE I

SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AT 25°

Added salt, moles per 1000 g. of H_2O	Soly., moles per 1000 g. of H_2O	Time of rotation, days	Log $(1/m_\pm)$	$\mu^{1/2}$	Added salt, moles per 1000 g. of H_2O	Soly., moles per 1000 g. of H_2O	Time of rotation, days	Log $(1/m_\pm)$	$\mu^{1/2}$
None	0.02680	4–10	1.3723	0.282					
In lead nitrate, $Pb(NO_3)_2$					In barium nitrate, $Ba(NO_3)_2$				
0.0020	0.02664	4	1.3634	0.293	0.002	0.02737	4	1.3664	0.297
.0050	.02644	4	1.3520	.307	.005	.02808	4	1.3509	.315
.0100	.02622	4	1.3340	.330	.01	.02883	4	1.3395	.341
.0200	.02612	4	1.3001	.372	.02	.03034	4	1.3173	.389
.0500	.02663	4	1.2202	.479	.05000	.03370	8	1.2717	.501
.1000	.02954	4	1.1169	.624	.09045	.03691	14	1.2322	.618
.1326	.03159	14	1.0612	.692	.1000	.03780	12	1.2219	.693
.2000	.03544	12	0.9757	.841	.2000	.04385	12	1.1574	.855
.3134	.04333	14	.8573	1.035	.2105	.04428	14	1.1532	.874
.5000	.05342	14	.7332	1.288	.3513	.05008	14	1.0997	1.097
.703	.06522	14	.6279	1.519	.4116[c]	.05337	14	1.0720	1.222
.9521	.07754	14	.5354	1.737					
1.654[a]	.1268	21	.3138	2.310					
1.964[a]	.1346	14	.2727	2.510					
In cadmium bromide, $CdBr_2$					In potassium bromide, KBr				
0.0010	0.02637	4	1.3674	0.286	0.001	0.02645	4	1.3714	0.283
.0020	.02591	4	1.3643	.289	.002	.02611	4	1.3718	.283
.0050	.02466	4	1.3539	.298	.0050	.02500	4	1.3734	.283
.0100	.02307	4	1.3321	.315	.0100	.02345	4	1.3732	.283
.0200	.01999	4	1.2977	.346	.0200	.02043	4	1.3737	.285
.0500	.01450	14	1.2059	.440	.0500	.01380	4	1.3594	.303
.1000	.01117	14	1.0860	.577	.1000	.00859	4	1.3097	.347
.1305	.01038	14	1.0281	.650	.2000	.00694	12	1.1661	.470
.2000	.00939	14	0.9280	.793	.3740	.00687	14	0.9955	.628
.3236	.00969	14	.7890	1.000	.3887[d]	.00700	14		
.5000	.01072	14	.6505	1.238	.5902[d]	.00707	14		
.5607	.01143	21	.6083	1.310	.8041[d]	.00740	14		
1.000	.01597	12	.3939	1.745	1.200[d]	.01137	14		
1.692	.02445	21	.1803	2.270					
4.182[b]	.06508	21	.2170	3.570					

[a] Solid phase, $PbBr_2$ and $Pb(NO_3)_2$.

[b] Solid phase, $PbBr_2$ and $CdBr_2 \cdot 4H_2O$.

[c] Solid phase, $PbBr_2$ and $Ba(NO_3)_2$.

[d] Solid phase, $KBr \cdot 2PbBr_2$.

The solubility of lead bromide has also been determined by Von Ende[3] and by Herz and Hellebrandt,[4] who expressed their results in moles per liter

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[3] Von Ende, *Z. anorg. Chem.*, *26*, 129 (1901).

[4] Herz and Hellebrandt, *Z. anorg. allgem. Chem.*, *130*, 188 (1923).

at 25°. Their results are summarized in Table II, in which the first column gives the concentration of the added salt, the second the solubility in the ordinary sense in moles per liter, the third the logarithm of the mean concentration and the fourth the square root of the ionic strength in concentration units.

TABLE II

SOLUBILITY OF LEAD BROMIDE IN AQUEOUS SALT SOLUTIONS AT 25°

Added salt, moles per liter, c	Soly., moles per liter	Log $1/c_{\pm}$	$\mu_c^{1/2}$
In nitric acid, HNO_3 (Von Ende[3])			
None	0.02628	1.3797	0.281
0.001	.02659	1.3746	.283
.01	.02735	1.3624	.304
.05[a]	.03025	1.3199	.375
.051	.03004	1.3216	.376
In calcium bromide, $CaBr_2$ (Herz and Hellebrandt[4])			
None	0 02625	1.3803	0.281
0.26	.00667	0.9073	.893
.52	.01205	.6217	1.255
1.04	.0438	.2289	1.803
1.565	.1175	−0.0411	2.246
2.085	.5187	−0.3827	2.795
In strontium bromide, $SrBr_2$ (Herz and Hellebrandt[4])			
0.26	0.00673	0.9060	0.883
.52	.01273	.6134	1.264
1.04	.04367	.2294	1.798
1.56	.1559	−0.0880	2.269
2.08	.5687	−0.4010	2.819
In barium bromide. $BaBr_2$ (Herz and Hellebrandt[4])			
0.225	0.00607	0.9624	0.832
.455	.01091	.6745	1.182
.91	.04443	.2639	1.692
1.38	.1604	−0.0609	2.150
1.835	.4140	−0.3077	2.597
In sodium bromide, NaBr (Herz and Hellebrandt[4])			
0.73	0.00860	0.7727	0.869
1.47	.02247	.4292	1.240
2.20	.07043	.1375	1.553
2.93	.1958	−0.1115	1.875
3.67	.3936	−0.2977	2.202
4.40	.7337	−0.4675	2.569

[a] 0.01 N HNO_3 + 0.04 N KNO_3.

Herz and Hellebrandt[4] also determined the solubility of lead bromide in calcium, strontium, barium, potassium and sodium chlorides, but the solid phase probably contained lead chloride. In their determinations in potassium bromide, the solid phase was probably a complex, in which case we cannot determine the concentration of the various constituents in the solution. The values of Table II are shown as the upper curves in Fig. 3.

Calculation of the Activity Coefficient from Solubility Measurements

The effective molality of a salt such as lead bromide in a mixture of electrolytes is determined by the mean molality of its ions rather than by the molality of either the lead ion or of the bromide ion. If the dissolved salt is in equilibrium with a solid salt, its activity is fixed and hence the mean activity coefficient is proportional to the reciprocal of the mean molality of the ion.[5] The ratio, therefore, of the reciprocal of the mean molality to the extrapolated reciprocal of the mean molality at zero concentration (proportionality factor of Lewis and Randall) gives the activity coefficient of the salt in the mixture.

Methods for Determining the Proportionality Factor.--Lewis and Randall[e] plotted the reciprocal of the mean molality, $1/m_\pm$ against the z^{th} root[7] of the ionic strength. The plots were found to give approximately straight lines, and by graphical extrapolation of the curves so obtained to zero ionic strength the value of the proportionality factor was directly found. These results did not differ greatly from those obtained by the methods we will describe.

In a second method, they obtained the ratio of the reciprocal of the mean molality of the unknown salt to known activity coefficients of salts of similar types at corresponding values of the ionic strength. These ratios were plotted against a function of the ionic strength and the limiting value of the ratio at zero ionic strength was taken as the proportionality factor.

The proportionality referred to above may be expressed in the form

$$\log \gamma + \text{const.} = \log (1/m_\pm) \qquad (1)$$

We have plotted in Fig. 1 the logarithm of the mean molality of thallous chloride[S] against the square root of the ionic strength, for various molalities of added salt. We also give, in Fig. 2, the final average curves for the

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[5] See ref. 2, Chap. 28. For the convenience of those who desire to follow the discussions of other authors, we give the notation now being used by several authors. (a) Lewis and Randall, ref. 2; (b) Bronsted, THIS JOURNAL, 42, 761 (1920); (c) Noyes, *ibid.*, 46, 1080, 1098 (1924); (d) Debye and Hiickel, *Physik.* Z., 24, 185 (1923).

NOTATION OF VARIOUS AUTHORS

	L. and R.	B.	N.	D. and H.
Activity of solvent	a_1	. . .	. . .	. . .
Activity of solute	$a_2, a_3, \ldots$	ξc	. . .	. . .
Activity of ions	$a_+, a_-, a_\pm$	ξ_1, ξ_2	. . .	. . .
Activity coefficient	$\gamma_+, \gamma_-, \gamma$	f_1, f_2, f	α_A, α_B	f_1, f_2, f_i
Moles per 1000 g. H_2O	m	. . .	c	γ'
Moles per liter	c	m	c	Y
Equiv. per liter	. . .	c	. . .	. . .
Valency	z_+, z_-	z_1, z_2	ν_A, ν_B	z_1, z_2, z_i
Ions per molecule	ν, ν_+, ν_-		z_A, z_B	ν_1, ν_2, ν_i

The symbol f was proposed and has always been used for the fugacity, which is an intensive quantity. The activity coefficient is a number without dimensions, and the symbol γ is preferred in accord with the custom of using a, β and γ for quantities without dimensions.

[6] Lewis and Randall, THIS JOURNAL, 43, 1112 (1921); ref. 2.

[7] $z_+ + z_- = z$, the sum of the valencies of the two ions formed by the dissociation; *e.* g., $z = 2$ for TlCl; $z = 3$ for $PbBr_2$ and $z = 4$ for $CaSO_4$. Lewis and Randall (unpublished) also plotted log $(1/m_\pm)$ against the z^{th} root of the ionic strength.

[8] See Randall and Chang, THIS JOURNAL, 50, 1535 (1928). The full data of other authors will be published in another place.

logarithm of the activity coefficient of typical strong electrolytes as taken from an unpublished summary of all data. In plotting Fig. 2, **1/2** log γ was taken for uni-bivalent salts, 1/3 log γ for uni-trivalent salts, 1/4 log γ for bi-bivalent salts, **1/6** log γ for bi-trivalent salts and 1/9 log γ for tri-trivalent salts, etc. In this way the curves of the salts of the various ionic types superimpose. This is also in accordance with the theoretical implications of the Debye and Hiickel theory.[9]

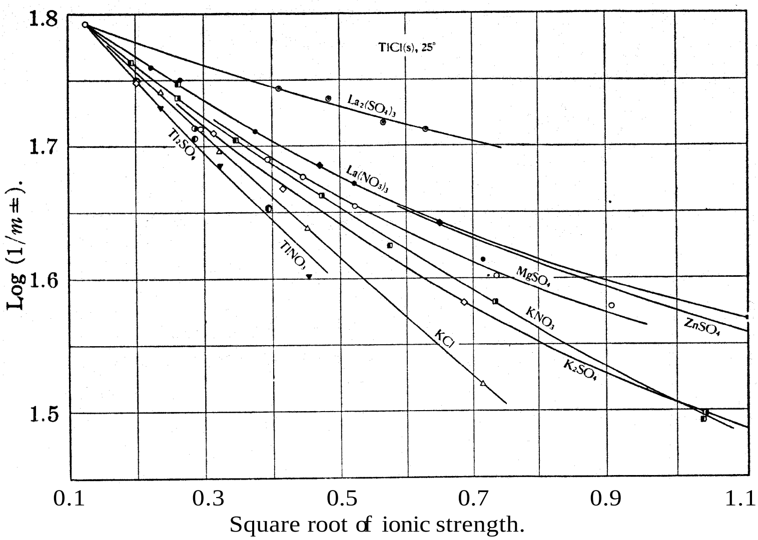

Fig. 1.—Solubility of thallous chloride in aqueous salt solutions at 25°.

If the added salt has the same characteristics as the saturating salt, that is, the same constants in a theoretical or empirical equation, or the same activity coefficient, then the curves of Fig. 1 would continue through the point of zero added salt, in the region of undersaturated solutions without a departure, but if the added salt has different characteristics, then there will be a more or less sharp departure. If Figs. **1** and **2** are made on transparent paper, using the same scale, then we may superimpose the plots, and if, as in the case of thallous chloride, the curve of log γ of thallous nitrate[10] superimposes on the curve of this same salt added to thallous

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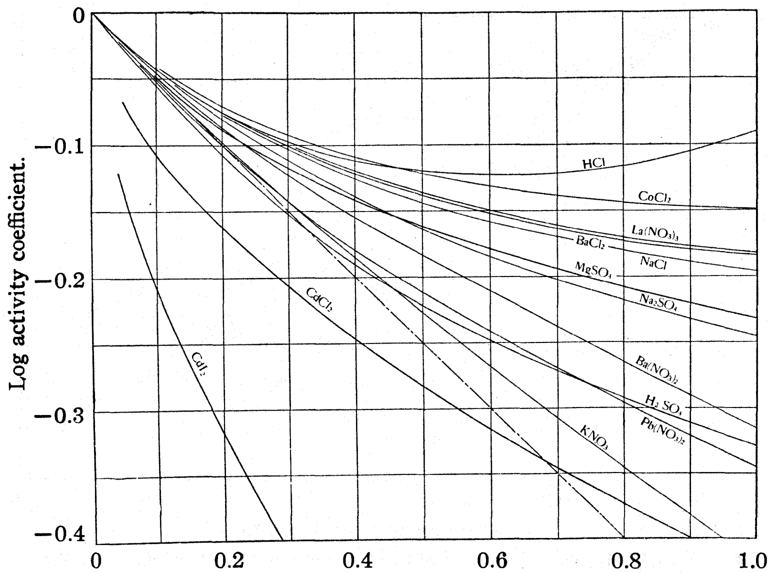
[9] See "The Theory of Strong Electrolytes, **A** Discussion," Trans. *Faraday Soc.*, 23,333–542 (1927).

[10] No actual measurements of the curve for thallous nitrate are available. (a) Lewis, THIS JOURNAL, 34, 1631 (1912), combined conductivity and transference data and showed that thallous and silver nitrates had smaller activity coefficients than potassium nitrate. (b) Onsager, *Physik.* Z., 28, 277 (1927), in his treatment of conductivity data, considers thallous nitrate to be an "associated" electrolyte. His functions stand in the same order as the activity coefficients of the salts. His curves show thallous chloride to be slightly lower than the nitrate.

chloride, we may confidently expect it to have about the same characteristics as thallous chloride and then choose the log proportionality factor as the intersection of the log y curve on the axis of the log $(1/m_\pm)$ curve. Thus we find log p.f. = 1.8630 ± 0.002 for thallous chloride. In some cases the curve of log $(1/m_\pm)$ will not superimpose upon any of the standard curves, but the curve may be between two of these curves. We then make such an estimate as will be most likely.



Pig. 2.—Activity coefficient of aqueous solutions of electrolytes.

In a number of cases concentrations have been expressed in moles per liter. In these cases we can convert the ionic strengths of the reference salts to ionic strengths in concentration units, y,. The activity of an ion is the same whether moles per liter or molality is used. If, therefore, we divide the activity by the concentration instead of by the molality, we obtain an activity coefficient in concentration units, γ_c, such that $a_2 =$ (my,)' $= (c\gamma_{c\pm})^\nu$. Reference plots of log γ_c against μ_c can be obtained by multiplying the values of log y by m/c for the temperature in question. For infinite dilution, therefore, log γ_c = 0.0013 at 25° and 0.0051 at 50°, if we are to retain our **definition**[11] that a, $= m_\pm$ at infinite **dilution.**[11] The difference between log y and log γ_c will, in general, be-

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[11] Debye and Hückel (ref. 5 d) have tacitly assumed the standard state so that the activity of an ion is equal to **its** concentration at infinite dilution. Thus their unit activity is equal to $1/c$ times the activity at a small concentration c, so small that $a_\pm' = c$. Their activity coefficient is, therefore, the number by which we multiply the concentration to find the activity referred to their tacitly assumed standard state. Because

come larger at greater concentrations. The value of log p.f. is obviously the same as when molalities are used, since the activity of the solid salt is constant and defined with reference to activities which become equal to molalities in infinitely dilute solutions.

Bronsted and LaMer[12] have plotted log S/S^0 against the square root of the ionic strength where S^0 is the solubility in pure water and S the solubility in the salt solution when no common ion is present. They then extrapolated to zero concentration and determined log γ by a method which is somewhat similar to the method here suggested.

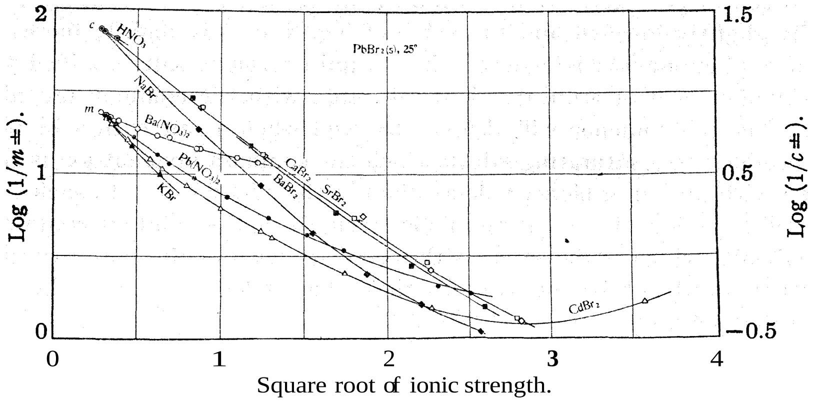

Fig. 3.—**Solubility** of lead bromide in aqueous salt solutions at 25°.

We show the values of 1/2 log $(1/m_{\pm})$ for lead bromide, taken from Table I, in Fig. 3 plotted against $\mu^{1/2}$. We have attempted to estimate the activity coefficient by superimposition of a portion of the data of Table I, drawn on the same scale as Fig. 2, upon that figure. The data for the activity coefficients of cadmium chloride, bromide and iodide are conflicting, and the curves drawn in Fig. 2 for these substances are provisional. We have been unable to apply the methods suggested above to the data for lead chloride, bromide or iodide and to obtain activity coefficients which would be consistent with the measured potentials of the halide electrodes and the measured free energies of the lead halides.

We have examined in the above manner all the available data for the

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the composition of their standard state varies with the temperature, that is, the number of moles of water in a liter changes with the temperature, it is not possible to use exact thermodynamic equations which are true only for constant composition. The difference in the free energy of an ion in the two standard states is given by the equation

Ion (a' = 1, Debye and Huckel) = Ion (a=1, Lewis and Randall);

$$\Delta F^\circ_{298} = 1364.9 \times \log 0.0013 = -1.7 \text{ cal.}; \quad \Delta F^\circ_{323} = -7.5 \text{ cal.} \qquad (2)$$

It is obviously most important in any tabulation of activities or of activity coefficients to so define the quantities that they will refer, as we have done, to a single standard state whether the experimental results are given in molalities or in concentrations.

[12] Bronsted and LaMer, THIS JOURNAL, 46, 555 (1924).

solubility of slightly soluble salts in the presence of electrolytes. The method of treatment here suggested seems to be justified if the saturating salt is not associated in the Bjerrum[13] sense, if the association is not large or if the solubility is very small. The application of the method to the data for thallous chloride represents perhaps the limit of the possibilities and, with salts such as lead iodide, erroneous results can easily be obtained.

An interesting phenomenon is observed in the case of the lowering of the solubility of lead bromide by small additions of potassium bromide. The effect of the common ion in lowering the solubility (in the old fashioned sense) is so great that the total ionic strength of the solution is actually slightly lowered and the value of log $(1/m_{\pm})$ is slightly increased. Such a phenomenon is general when a uni-univalent salt is added to a uni-bivalent salt or a uni-trivalent salt, etc., with the common univalent ion. The phenomenon will also be observed when a salt with a bivalent ion is added to a saturating salt in which the common bivalent ion is combined with an ion of higher valence than in the added salt. In such cases the value of log $(1/m_{\pm})$ at the ionic strength of the solution containing added salt, which is the same as the ionic strength of the pure saturated solution, need not be the same as the value of log $(1/m_{\pm})$ of the pure saturated solution.

Summary

The solubility of lead bromide in aqueous salt solutions has been determined at 25°.

A refined technique for such determinations is described.

The determination of the activity coefficient by graphical treatment of solubility data is discussed. Specific applications of a convenient graphical method are made in the case of thallous chloride and lead bromide.

The solubility method, while satisfactory when the saturating salt is "non-associated," or when the solubility is very small, may lead to considerable errors with fairly soluble "associated" substances such as lead bromide.

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[13] Bjerrum, *Det. Kgl. Danske Videnskab Math -fys. Medd*, 7, No. 9 (1926).

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

THE SOLUBILITY OF THALLOUS CHLORIDE IN WATER AND AQUEOUS SOLUTIONS OF MAGNESIUM SULFATE AND LANTHANUM NITRATE AT 25°

BY MERLE RANDALL AND K. S. CHANG

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The solubility of thallous chloride has been determined in water and aqueous solutions of magnesium sulfate and lanthanum nitrate at 25°, using the same apparatus as that used in the previous investigation.[1]

The thallous chloride was prepared by metathesis, washed with dilute hydrochloric acid and rotated with water to a constant solubility. An older sample from a previous investigation gave the same solubility. The salts were recrystallized from high grade materials and the purity was checked by analysis.

All concentrations are expressed in moles per 1000 g. of water in vacuum. Weighed samples of the saturated solution were titrated with standardized silver nitrate solution (weight buret). The end-point was determined without indicator, using Tyndall's optical test.

Equilibrium was approached from undersaturation and supersaturation in each case. The solid phase was analyzed after the experiments with the most concentrated solutions of added salts and found to be thallous chloride in both cases.

The results are given in Table I. The first column gives the molality of the added salt, the second the molality of the thallous chloride, the third the square root of the ionic strength, the fourth the logarithm of the

TABLE I

SOLUBILITY OF THALLOUS CHLORIDE IN AQUEOUS SOLUTIONS OF MAGNESIUM SULFATE AND LANTHANUM NITRATE AT 25°

Added salt	m	Soly.	$\mu^{1/2}$	Log $(1/m_\pm)$	Log γ
None	0.00000	0.01611	0.1269	1.7929	−0.070
$MgSO_4$	.01708	.01920	.2958	1.7127	− .150
	.03364	.02042	.3937	1.6899	− .173
	.04384	.02106	.4454	1.6765	− .187
	.06259	.02214	.5220	1.6548	− .208
	.1291	.02504	.7358	1.6014	− .262
	.1994	.02641	.9078	1.5782	− .285
	.3529	.02878	1.2002	1.5409	− .322
$La(NO_3)_3$	.005215	.01740	0.2224	1.7594	− .104
	.008808	.01778	.2657	1.7500	− .113
	.02024	.01946	.3754	1.7109	− .152
	.04180	.02129	.5216	1.6718	− .192
	.08166	.02433	.7171	1.6138	− .249
	.1970	.02697	1.1000	1.5692	− .294

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[1] Randall and Vietti, THIS JOURNAL, 50, 1526 (1928).

reciprocal of the mean molality of the thallous and chloride ions and the last the activity coefficient of the thallous chloride in the mixture.

These results have been reviewed in the previous paper. The specific gravity of the saturated solution was found to be 1.0034 and its density 1.0004. Bray and Winninghoff[2] give 0.9994 as the density of the saturated solution, which corresponds to a solubility of 0.01615 mole per 1000 g. of water. Butler and Hiscocks[3] found the same solubility, 0.01607 mole per liter, as that found by Bray and Winninghoff, but found the density to be 1.0004, from which the solubility is 0.01612 mole per 1000 g., in agreement with our value.

Summary

The solubility of thallous chloride in water and aqueous magnesium sulfate and lanthanum nitrate solutions and the density of the saturated aqueous solution at 25° have been determined.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS. I. THE DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS OF THE CHLOROBENZENES IN BENZENE AND IN HEXANE[1]

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Some years ago it was recognized that the calculation of the electric moments of molecules from dielectric constants might provide valuable aid in solving the complex problems of molecular structure. An approximate method of calculation was devised and applied to data on pure substances already existing in the literature to obtain the moments of a large number of molecules.[3]

It was evident, however, that many molecules which were surrounded by strong fields of force did not lend themselves to this calculation. The experimental work, which was then being initiated in the Palmer Physical

[2] Bray and Winninghoff, THIS JOURNAL, 33, 1663 (1911).

[3] Butler and Hiscocks, J. *Chem. Soc.*, 129,2554 (1926).

[1] Papers based upon the data of the present contribution were presented before the Physical and Inorganic Division and before the Organic Division of the American Chemical Society in Philadelphia, September, 1926. The results of the measurements upon the substituted benzene compounds have been applied in a study of the structure of the benzene ring, Smyth and Morgan, THIS JOURNAL, 49,1030 (1927).

[2] DuPont Fellow in Chemistry, 1926-27.

[3] (a) Smyth, *Phil. Mag.*, 45, 849 (1923); (b) 47, 530 (1924); (c) THIS JOURNAL, 46,2151 (1924); (d) 47,1894 (1925).

Laboratory, was, therefore, directed to the measurement of the dielectric constants and densities of liquid mixtures in which a molecule with a strong field of force could be surrounded by molecules with weak fields. It is our aim to use these data not only for the calculation of electric moments and the study of molecular structure, but also for the investigation of the effect of the force fields of the molecules upon one another in causing molecular association and deviations from ideal behavior.

Theoretical

As the nature of the electric moment and its relation to molecular structure has been discussed in the papers already referred to, only the equations immediately necessary will be given here. The molar polarization P of a substance in which the molecules are free to assume a perfectly random orientation may be represented by the Debye equation,[4] written in the following form

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} = \frac{4\pi}{3}N\gamma + \frac{4\pi N}{9k}\frac{\mu^2}{T} \qquad (1)$$

in which ϵ = the dielectric constant; M = the molecular weight; d = the density; N = the number of molecules in a gram molecule = 6.061 X 10^{23}; γ = the molecular polarizability; k = the molecular gas constant = 1.372 × 10^{-16}; μ = electric moment of a single molecule; and T = the absolute temperature. $(4\pi/3)N\gamma$ is the polarization due to shifts of charges in the molecule induced by the external field. It is commonly calculated as the molar refraction for light of infinite wave length, MR, = $[1-\lambda_0^2/\lambda^2]$ $[(n^2-1)M]/[(n^2+2)d]$, where n is the index of refraction for light of wave length X and λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region. The quantity thus calculated by extrapolation from the visible region takes account only of the electronic shifts induced, and is, therefore, designated as P_E, but atoms and groups of atoms or radicals may shift under the influence of an external field in such a way as to contribute somewhat to the polarization.[5] We may, therefore, write $(4\pi/3)N\gamma = P_E + P_A$, where P_A, the difference between P_E and the total polarization induced in the molecules may be termed the atomic and radical contribution to the polarization. Setting $(4\pi N/9k)$ (μ^2/T), the contribution of the moments of the molecules oriented by the external field, = P_M, we have $P = P_E + P_A + P_M$.

When the molecules are rigidly bound in the solid state and, therefore, unable to orient themselves in an applied field, $P_M = 0$. By determining the polarization P in the solid state, calculating P_E from optical data, and

[4] Debye, *Physik. Z.*, 13, 97 (1912); "Handbuch der Radiologie (Marx)," Akademische Verlagsgesellschaft M. B. H., Leipzig, 1925, VI, p. 619.

[5] Ebert, *Z. physik. Chem.*, 113, 1 (1924); 114, 430 (1925).

setting $P_M = 0$, Errera[6] has obtained values of P_A for a number of substances. When the molecules in a liquid affect one another to such an extent that they are not oriented at random in the absence of an external field, the expression for P_M may no longer be expected to hold. If the molecules are oriented in such a way that the axes of their electric doublets tend to point in the same direction, P_M is increased, while if these doublets tend to oppose one another, it is decreased. This arrangement of the doublets relative to one another may be anything from a very slight orientation of the molecules to an association in the form of molecular complexes.

The molar polarization of a mixture of two substances, 1 and 2, is given by the expression[4]

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d} = c_1P_1 + c_2P_2 \tag{2}$$

in which 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. As $c_1 = 1-c_2$, it is evident that P_{12} is a linear function of c_2 when P_1 and P_2 are constant. If P_1 is constant but P_2 varies with concentration the latter may be calculated by writing the equation in the form

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1 \tag{3}$$

In the study of binary mixtures, one may choose a liquid 1, such as benzene or hexane, the molecules of which have no moment and may be described as non-polar, and, for liquid 2, a substance[3c] the molecules of which have large moments and will be referred to as polar. In such mixtures, P_1 may be assumed to be approximately constant, since its value is equal to $P_E + P_A$, which are dependent upon intramolecular behavior and vary little with concentration. The variation of P_2 with concentration may then be taken as an indication of the character and extent of the molecular orientation or association of substance 2.

The equation of Debye was criticized by exponents of the older quantum theory, but applications of the newer quantum mechanics to simple polyatomic molecules have given equations from which results practically identical with those of the Debye equation may be obtained and Van Vleck[7] has recently given a general proof of the equation on the basis of the new mechanics. Experimental investigations have shown[8] that, in a simplified form, the equation represents admirably the temperature variation of the dielectric constants of a number of dipole gases but, presum-

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[6] Errera, *Physik. Z.*, 27, 764 (1926).

[7] Van Vleck, *Phys. Rev.*, 29, 727 (1927); 30, 31 (1927).

[8] (a) Jona, *Physik. Z.*, 20, 14 (1919); (b) Zahn, *Phys. Rev.*, 24, 400 (1924); (c) Smyth and Zahn, THIS JOURNAL, 47, 2501 (1925); (d) Sänger, *Physik. Z.*, 27, 556 (1926); 28, 455 (1927).

ably, because of lack of complete freedom of the molecules, it has not been found generally satisfactory when applied to a pure dipole liquid.

Apparatus and Procedure

The measurements of dielectric constant were made with a capacity bridge, which was used in preference to newer methods involving coupled oscillating circuits because of the frequent failure of the latter to distinguish between capacity and conductance, which failure may introduce a serious error into apparently precise results. It is probable, however, that a newer circuit of established accuracy may be used in later measurements.

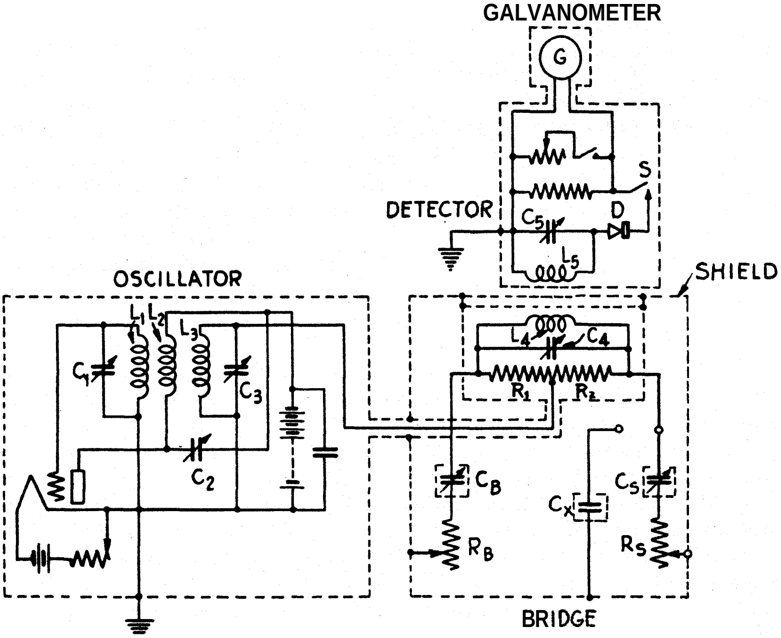

Fig. 1.—Capacity bridge.

As the apparatus possessed certain novel features, a diagram is given in Fig. 1, in which electric shields are represented by dotted lines. The oscillator, bridge and detector were each in separate galvanized iron boxes, fitting closely against one another and grounded. The oscillator tube was a Western Electric 216-A type operated with 135 volts on the plate and giving a direct current in the plate circuit of approximately 30 milliamperes. The three coupling coils (L_1, L_2, L_3) were wound beside one another on the same fiber core. The setting of the variable condensers (C_1 and C_2) across the fixed grid and plate inductances (L_1 and L_2) determined the frequency of the oscillations, 5×10^5 cycles corresponding to a wave length of 600 meters being adopted as suitable for the bridge and checked occasionally by means of a wave meter. The condensers (C_3 and C_4, C_5) across the power and detector coils (L_3 and L_4, L_5) were for tuning, by means of which it was possible to increase two- or three-fold the deflection of the galvanometer used as null instrument for a given capacity change in either arm of the bridge. The power was brought from the oscillator to one corner of the bridge by a heavy, shielded wire, the circuit being completed by grounding the opposite corner of the bridge. In order to maintain the symmetry of the bridge, this power lead was carried beneath the bottom of the box containing the bridge and brought vertically up to the corner shown between R_1 and Rp. The bridge consisted of two resistance arms, R_1, R_2, of 1000 ohms each, specially wound non-inductively on the same Bakelite cylinder and shielded from the rest of the bridge, and two capacity arms, the balancing condenser C_B, a 2000 $\mu\mu$f shielded air condenser, and the standard condenser C_S, a General Radio Company type 222 precision instrument of 1500 $\mu\mu$f capacity. These condensers were connected to the grounded shield through General Radio Company decade resistance boxes, R_B and R_S, non-inductively wound. The resistance in series with C_B was used to balance any conductance in the measuring cell C_x, which could be connected in parallel with C_S, while that in series with C_S was rarely used, having been inserted largely with the object of maintaining the symmetry of the bridge as far as possible. The ends of R_1 and R_2, remote from one another and forming opposite corners of the bridge were connected through a small honey-comb coil, L_4, loosely coupled through a grounded electrostatic shield to another coil, L_5, current through which was rectified by a crystal detector, D, and passed through a Leeds and Northrup high sensitivity galvanometer G, minimum deflection of which indicated balance of the bridge. A switch. S, which could be operated without opening the box, was used to close the detector circuit. The galvanometer was critically damped and a variable shunt was used to protect the galvanometer while bringing the bridge approximately to balance.

A balance of the bridge was obtained when the capacity and conductance were the same in each arm. When the conductance in the opposite arms was different there was a current flowing in the galvanometer, even though the capacity in both arms was the same.

The method of operation was to vary the standard condenser and the balancing resistance until practically zero current was obtained in the galvanometer, both conductance and capacity being then balanced. The condenser containing the liquid to be measured was then connected in parallel with the variable standard condenser and the bridge balanced again by varying the standard condenser and balancing resistance. The capacity of the measuring condenser was equal to the change of the variable standard condenser required to bring the bridge back to balance. With the liquids used in this work, it was unnecessary to change the balancing resistance by more than a few tenths of an ohm.

The measuring condenser C_x consisted of two concentric gold-plated brass cylinders closed at both ends, separated by a distance of 1 mm. on the sides, and insulated from each other and held rigidly by quartz disks set in bushings at the ends. A slightly larger gold-plated cylinder with a cover served as container. Twenty-five cc. of liquid were required to fill this container and the air capacity of the condenser was 34 $\mu\mu$f.

The capacity of the measuring condenser was made up of two parts, the fixed capacity due to the leads and insulation, which did not vary with the dielectric constant of the liquid in the cell, and the capacity between the plates, which was directly proportional to the dielectric constant of the liquid in the condenser. The condenser was calibrated by determining its capacity filled with air and again filled with a liquid whose dielectric constant was well known. The calibrating liquid was benzene, for which a mean value of $\epsilon = 2.273$ at 25° was adopted from the work of Isnardi,[9] Graffunder[10] and Lertes.[11]

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[9] Isnardi. *Z. Physik*, 9,153 (1922).

[10] Graffunder, Ann. *Physik*, 70,225 (1923).

[11] Lertes, *Z. Physik*, 6,257 (1921).

Ether, toluene, chloroform and carbon tetrachloride were also measured with a view to calibration and the agreement obtained with the most probable values for the dielectric constants of these substances was satisfactory, but, as the benzene value appeared to be the most accurate, it seemed best to rely wholly on it.

The precision condenser C_S, after being fixed in position in the bridge, was recalibrated in terms of a fixed capacity, that of the empty measuring cell serving as a convenient unit, and this calibration was checked from time to time.

The densities of the liquids were determined with an Ostwald-Sprengel pycnometer, the ends of which were fitted with caps to prevent evaporation. For measurements at 0°, the cell and pycnometer were immersed in cracked ice and water, and, at 25 and 50°, in carefully regulated thermostats. The probable error of the dielectric constant measurements was 0.5% and of the density determinations 0.03%.

Preparation of Materials

The hexane used was Eastman Kodak Company petroleum hexane, b. p. 65–70". The first lot was treated with acid and alkaline permanganate as recommended by Castelli and Henri[12] and then fractionated. The middle fraction differed from the unpurified material so little in its dielectric properties that, in the work which followed, the untreated hexane was used.

Merck's crystallizable benzene was shaken three times with concentrated sulfuric acid and then with water. It was dried over phosphorus pentoxide and fractionated.

The monochlorobenzene was shaken several times with concentrated sulfuric acid, then with water, dried over fused calcium chloride and fractionated.

The dichlorobenzenes were Eastman Kodak Company products. The ortho and meta isomers were fractionated under reduced pressure, only the middle fraction being used. The para compound was crystallized twice from ethyl alcohol and thoroughly dried over calcium chloride.

Results

Table I gives the experimentally determined dielectric constants and densities of the liquid mixtures at 0, 25 and 50°, together with the values

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS OF BINARY MIXTURES

Mole fraction of	ϵ			d			P_{12}		
	0°	25°	50°	0°	25°	50°	0°	25°	50°
C_6H_5Cl in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0786	2.710	2.621	2.518	0.9214	.8973	.8713	31.80	31.58	31.13
.1988	3.140	2.994	2.853	.9485	.9227	.8963	37.28	36.80	36.16
.4007	3.879	3.659	3.443	.9986	.9712	.9441	45.09	44.45	43.70
.6020	4.650	4.332	4.050	1.0435	1.0178	.9907	52.00	51.14	50.37
.7048	5.039	4.665	4.339	1.0663	1.0393	1.0125	55.10	54.20	53.30
1.000	6.088	5.628	5.226	1.1272	1.1006	1.0737	62.84	62.06	61.25

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[12] Castelli and Henri, *Bull. soc. chim. biol.*, 6, 299–302 (1924).

TABLE I (*Concluded*)

Mole fraction of	ε			*d*			P_{12}		
	0°	25°	50°	0°	25°	50°	0°	25°	50°
o-$C_6H_4Cl_2$ in C_6H_6									
0	...	2 273	2.226	....	0.8727	0.8458	...	26.63	26.84
0 0205	...	2.453	2.373	....	.8837	.8570	...	29.34	29.10
.054	2.873	2.724	2.607	0.9243	.9022	.8792	33.97	33.05	32.44
.1156	3.331	3.153	2.998	.9621	.9328	.9063	39.11	38.54	37.93
.2015	4.023	3.777	3.561	1.0016	.9748	.9476	46.06	45.34	44.67
.5010	6.520	5.988	5.547	1.1367	1.1094	1.0826	64.22	63.50	62.73
1.000	11.130	9.930	8.900	1.3251	1.2973	1.2699	85.53	84.80	83.90
m-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.0372	2.497	2.414	2.342	0.9184	.8916	.8648	29.22	28.97	28.80
.1008	2.719	2.629	2.533	.9494	.9234	.8966	32.61	32.40	32.04
.2703	3.283	3.130	2.989	10314	1.0033	.9761	40.48	40.02	39.48
.6837	4.552	4.254	3.997	1.2014	1.1702	1.1427	56.47	55.67	54.76
1.000	5.403	5.039	4.703	1.3085	1.2799	1.2523	6680	65.90	64.80
p-$C_6H_4Cl_2$ in C_6H_6									
0	...	2.273	2.226	....	0.8727	0.8458	...	26.63	26.84
0.1354	2.372	2.323	2.266	0.9673	.9407	.9135	28.34	28.49	28.37
.1483	2.389	2.341	2.276	.9735	.9466	.9198	28.70	28.79	28.65
.3860	...	2.359	2.313	....	1.0555	1.0280	...	30.92	31.00
.6741	...	...	2.369	....	...	1.1421	...	...	34.16
.7335	...	...	...	....	....	1.1703	...	...	...
C_6H_5Cl in C_6H_{14}									
0.0	1.960	1.908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0293	2.060	1.989	1.922	.6990	.6761	.6528	32.47	31.87	31.28
.0792	2.201	2.122	2.039	.7177	.6940	.6707	35.13	34.59	33.83
.1470	2.419	2.312	2.221	.7430	.7191	.6952	38.89	38.07	37.43
.2903	2.870	2.727	2.543	.7981	.7748	.7505	45.14	44.26	42.61
.4979	3.690	3.453	3.249	.8860	.8601	.8353	52.98	51.94	50.92
,7540	4.824	4.467	4.153	1.0027	.9770	.9511	59.28	58.19	57.13
,8477	5.370	4.953	4.602	1.0502	1.0222	.9962	61.24	60.36	59.40
1.000	6.088	5.628	5.226	1.1278	1.1008	1.0741	63.03	62.26	61.62
o $C_6H_4Cl_2$ in C_6H_{14}									
0	1.960	1908	1.839	0.6882	0.6656	0.6426	30.32	30.07	30.04
0.0255	2.100	2.035	1.966	.7037	.6805	.6572	33.50	33.14	32.58
.0739	2.382	2.292	2 190	.7327	.7084	.6848	39.09	38.51	37.63
.1320	2.783	2.630	2.503	.7684	.7425	.7184	45.73	44.66	43.73
.3406	4.370	4.030	3.744	.8935	.8715	.8463	63.30	61.66	60.29
.5881	6.498	5.873	5.384	1.0527	1.0238	.9978	74.88	73.75	72.60
1.000	11.130	9.930	8.900	13251	1.2973	1.2699	85.53	84.80	83.90
m-$C_6H_4Cl_2$ in C_6H_{14}									
0	1.960	1.908	1.839	0.6882	0 6656	0.6426	30.32	30.07	30.04
0.0204	2.024	1,969	1.900	.7056	.6818	.6587	31.57	31.36	30.30
.0245	...	...	...	.7061	.6840	.6608	...	...	...
.0684	2.168	2.087	2.014	,7318	.7085	.6850	34.64	34.03	33.40
.2084	2.602	2.480	2.337	.8140	.7926	.7682	42.24	41.21	39.64
.4324	3.270	3 090	2 948	.9477	.9235	.8980	51.22	50.07	49.36
1.000	5.403	5 039	4.70'3	1 3085	1 2799	1 2523	66 80	65.90	64.80

of the polarization, P_{12}, calculated by means of equation (2). Typical curves showing the variation of these quantities with the composition of the mixture are given in Figs. 2, 3 and 4. For the sake of brevity, the actual values calculated for P_2, the molar polarization of the polar substance, at the different concentrations are omitted but the results obtained for benzene solutions at 50° are plotted in Fig. 5. The P_2 curves obtained for the solutions in hexane were similar in character to those for the ben-

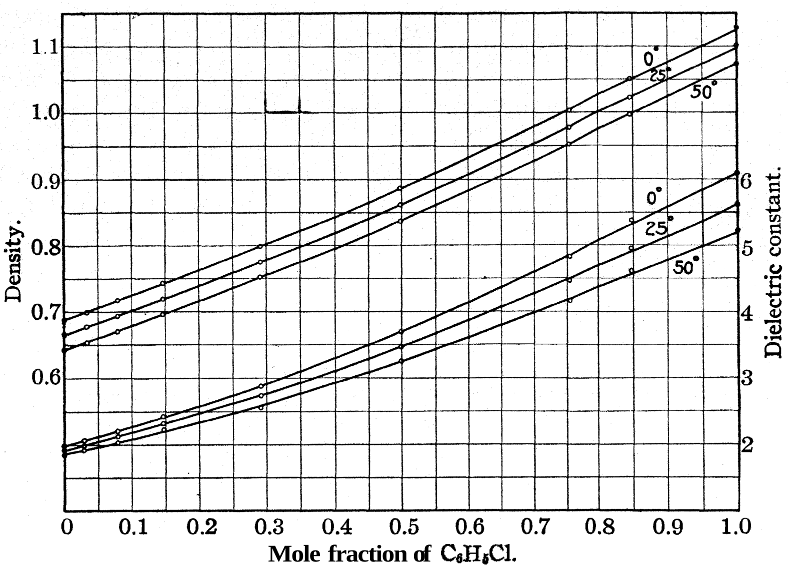

Fig. 2.—Densities and dielectric constants of chlorobenzene–hexane mixtures.

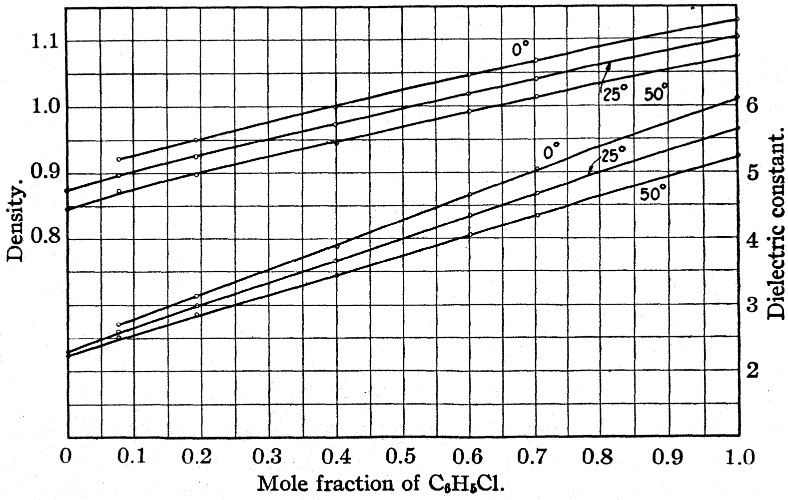

Fig. 3.—Densities and dielectric constants of chlorobenzene–benzene mixtures.

zene solutions, which are shown in preference to the former because p-dichlorobenzene was measured only in benzene. The values of P_2 at infinite dilution at 25° obtained by extrapolation to zero concentration ($c_2 = 0$) of the polar substance are given in Table II as P_∞, together with the values of P_E calculated from data in "International Critical Tables" in agreement with the calculations of Errera,[6] P_A obtained by Errera for the dichlorobenzenes, P_M calculated as $P_M = P_\infty - (P_E + P_A)$, and the electric moment calculated from P_M. Solid monochlorobenzene has not been investigated but an approximate value, 3.3, may be calculated for P_A from results to be described in our next paper. This value is, therefore, inserted here and used to obtain P_M and μ.

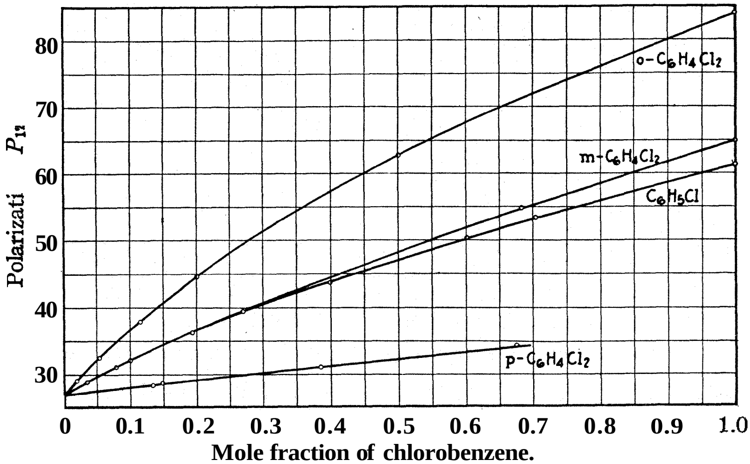

Fig. 4.—Polarization (P_{12}) of mixtures of chlorobenzenes with benzene at 50°.

TABLE II

POLARIZATION CONTRIBUTIONS AT 25° AND ELECTRIC MOMENTS OR THE CHLOROBENZENES

	P_∞	P_E	P_A	P_M	$\mu \times 10^{18}$
C_6H_5Cl	83.6	29.9	3.3	50.4	1.56
o-$C_6H_4Cl_2$	145	34.4	5.8	104.8	2.25
m-$C_6H_4Cl_2$	84.3	34.6	4.4	45.3	1.48
p-$C_6H_4Cl_2$	37.8	34.8	3.4	0	0

Discussion of Results

The value for the moment of monochlorobenzene agrees well with the figure 1.58 × 10^{-18} recently published by Höjendahl[13] and by Williams and Krchma,[14] who, being unable to take into account the small quantity P_A, obtained a slightly high value. It also differs by less than the possible

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[13] Höjendahl, *Nature*, 117,892 (1926).

[14] Williams and Krchma, THIS JOURNAL, 49,1676 (1927).

error from the value, 1.52 × 10^{-18}, obtained by the more accurate method to be described in Part II of this series. **All** the values of the moment in Table II are, of course, slightly lower than those first published[1] when no data were available for the calculation of P_A. The values of the polarizations of pure o- and m-dichlorobenzene are in satisfactory agreement with those of Errera and that for P, of the para compound is identical with Errera's value. For this latter compound, P_M is given as 0 instead of the figure —0.4 actually obtained, which is less than the probable error and has no apparent physical significance. The values for P, of the ortho and the meta compound and consequently of the moments are distinctly higher than those obtained by Errera, whose extrapolation was made at but one temperature and based upon measurements in only one solvent.

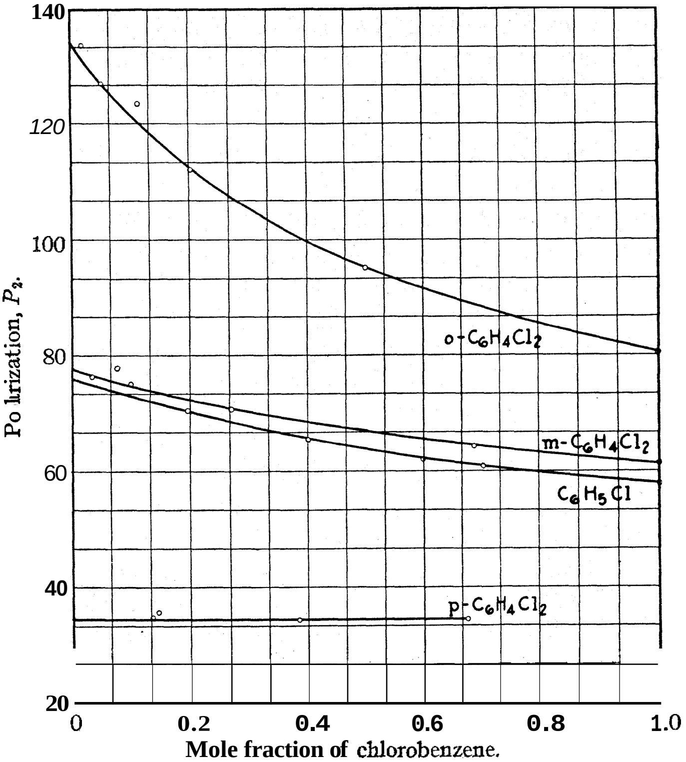

Fig. 5.—Polarization (P_2) of chlorobenzenes in benzene solutions at 50°.

The curves (Figs. 2 and 3 show typical curves) representing the variation of the dielectric constant and the density with the mole fraction c_2 of the polar substance are, in some cases, very nearly linear, but the dielectric constant curves usually possess marked curvature. The departure from linearity of both the dielectric constant and the density curves evidently depends upon the character not only of the polar substance but also of the non-polar. For a given set of mixtures at different temperatures, the density curves run much more nearly parallel than the dielectric constant curves, which spread apart with increasing content of the polar substance because of the high temperature coefficient of the latter indicated by equation (1). In Fig. 4 *p*-dichlorobenzene, which has no electric moment, is the only substance showing a linear variation of P_{12} with c_2 as required by equation (2) if P_1 and P_2 are constant and independent of c_2. The departure from linearity of the other curves is attributable to decrease in P_2, the polarization of the polar substance, because of increase in molecular orientation with increasing concentration. Monochlorobenzene and m-dichlorobenzene, which have nearly equal moments, have very similar curves, that for the latter lying a little higher in the more concentrated region because of its greater chlorine content, which gives a higher value for MR,. The relations are clear in Fig. 5, in which the P_2 curve for the para compound is a horizontal straight line showing independence of concentration when the moment is zero. For the other compounds, P_2 decreases rapidly with increasing concentration, particularly in the dilute region, the decrease being greatest in the case of the ortho compound which has the largest moment. The values at different temperatures, which have been omitted for the sake of brevity, show that P_2 decreases with rising temperature more rapidly in the dilute solutions than in the concentrated, where increasing thermal agitation gives increased freedom to the molecules, which can thus orient more freely in the applied field.

It may be concluded that the molecules of the chlorobenzenes tend to orient themselves in such a way that neighboring doublets oppose one another, thereby decreasing the polarization. This effect is greater, the greater the moment of the molecule, the lower the temperature and the smaller the distance between the doublets, that is, the greater the concentration. Measurements upon solutions of acetic acid in benzene and in ether, which, because of their preliminary character and uncertain interpretation, are not included in the present paper, indicate that, as might be expected, not only the magnitude of the field of force around the single molecule but also steric influences and highly localized valence forces may play an important part in determining the behavior of the molecules.

The writers wish to express their indebtedness to the National Academy of Sciences for a grant from the Joseph Henry Fund, and to thank Professor K. ?'. Compton for his helpful interest in the work.

Summary

A capacity bridge for the measurement of dielectric constants is described and the dielectric constants and densities of solutions of chloro-

benzene and o-, m- and p-dichlorobenzene in benzene and in hexane are given.

The polarization and electric moments calculated indicate that, as might be expected, the molecules affect one another more strongly, the greater their moments, the greater their concentrations and the lower the temperature.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY]

THE DIELECTRIC POLARIZATION OF LIQUIDS.
II. THE TEMPERATURE DEPENDENCE OF THE POLARIZATION IN CERTAIN LIQUID MIXTURES[1]

BY C. P. SMYTH AND S. O. MORGAN[2]

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As the results reported in Part I showed that the effect of polar molecules upon one another in dilute solution varied greatly with concentration and with temperature, it was evident that accurate determinations of dielectric constant and density over a wide range of temperature were needed.

Apparatus

The apparatus described in Part I was modified, although the same capacity bridge with the same wave length of 600 meters was used. The Western Electric 216-A tube in the oscillator was replaced by a 5-watt 104-DW power tube, upon the plate of which 250 volts were applied by means of a high speed motor generator. This increased the accuracy of the bridge balance by supplying more current. The measuring cell used in the earlier work was replaced by a condenser of approximately 200 $\mu\mu$f. capacity, which greatly reduced the relative error of a capacity measurement. Since the capacity of this cell when filled with a liquid of high dielectric constant was greater than that of the precision condenser which was used to measure it, a 1000 $\mu\mu$f. variable air condenser of the same type as that used in the balancing arm of the bridge was so arranged that, by means of interchangeable brass rods dipping into cups filled with mercury, it could be connected in series with the cell or in parallel with the precision condenser or could be totally disconnected. When the capacity of the cell was too great to be measured by direct substitution on the precision condenser, this variable air condenser was set at a convenient value, measured on the precision condenser, and then connected in series with the cell. The capacity of the cell and condenser, thus reduced by the series connection, was measured on the precision condenser and the capacity of the cell alone then calculated.

The measuring cell (Fig. 1) was designed in such a way as to have large electrical capacity, small internal volume and small temperature lag. It was made up of three concentric platinum cylinders (A), with diameters 1.95, 1.80 and 1.64 cm., respectively, open at the ends. The outer and inner cylinders, which were 9.2 cm. long, were con-

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[1] A paper based upon the results of the present contribution was presented before the Physical and Inorganic Division of the American Chemical Society in Richmond, April, 1927.

[2] DuPont Fellow in Chemistry, 1926–27.

nected together and to ground while the middle cylinder, which was 8 cm. long, was centered between them and held at a distance of 0.05 cm. from them by small blocks of mica placed at the top and bottom. The entire condenser was enclosed in a vessel consisting of two concentric glass tubes sealed together at top and bottom, the outer tube being but slightly larger than the outer platinum cylinder and the inner tube fitting inside the innermost platinum cylinder. The leads, which were platinum wires welded to the cylinders, were brought out through heavy capillary tubes (B, B'), spread to a distance of 8 cm. from one another to reduce the mutual inductance and capacity of the leads, the ends of which were sealed into the bottoms of mercury filled cups (C, C') to make connections with the bridge.

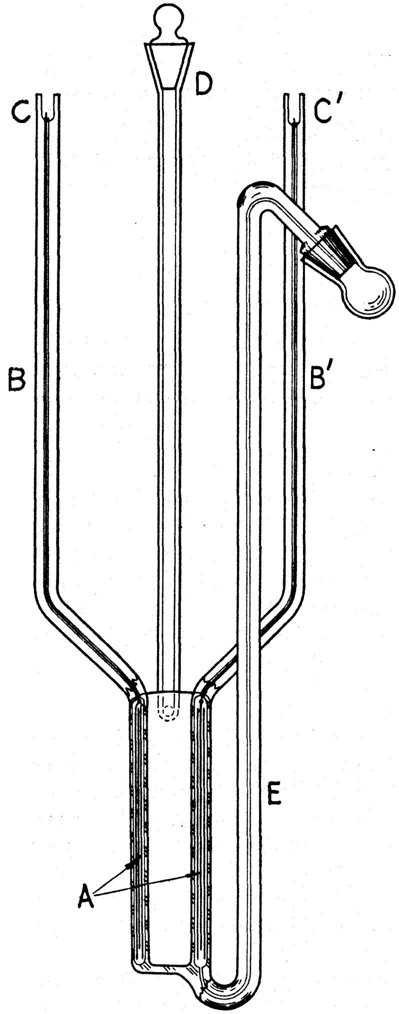

Fig. 1.—Measuring condenser.

These tubes (B, B'), as well as the inlet and outlet tubes (D and E), extended 22 cm. above the cell, which could, therefore, be immersed well below the surface of a constant temperature bath. The cell, which held only 18 cc., was filled through the inlet tube D, which was provided with a ground glass stopper, and was emptied by applying air pressure to D and forcing the liquid through the capillary outlet tube E, which could be closed with a ground glass cap over the end. The cell was normally kept in a vertical position and, if necessary, could be filled and emptied without removal from the constant temperature bath. It was dried by means of a current of filtered, dry air. As the cross section of the cell was a ring, it was in contact with the bath liquid both inside and out. The grounded outer and inner cylinders of the condenser served as shielding for the shorter cylinder between them. Stray, fixed and lead capacities were so reduced that the capacity which depended upon the substance in the cell was 96% of the total when the cell contained air. The variation of the air capacity of the condenser over the temperature range -90 to $+60°$ was no greater than the error of the measurement. The cell was standardized as in the earlier work by determining its capacity when filled with air and with benzene ($\epsilon = 2.273$ at 25°), the standardization being checked from time to time.

The constant temperature bath[3] was a Pyrex Dewar tube, 18" tall by 4" inside diameter, which, for temperatures below $-90°$, was filled with petroleum ether, between -90 and $+90°$, with toluene, and, above $+90°$, with kerosene. Immersed in the bath was a small copper cylinder into which liquid air could drip through a small,

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[3] Compare Walters and Loomis, THIS JOURNAL, 47, 2302 (1925).

straight tube and out of which the evaporated air could escape through a spiral tube. A vacuum jacketed siphon carried the liquid air to this cooling device from a stoppered 2-liter Pyrex Dewar flask, pressure being developed by the evaporation of liquid in the flask and regulated by attachment to a tube passing through the stopper of capillary tubes of varying bore and length. The copper cylinder was surrounded by a small heating coil which was used to raise the temperature of the bath when desired.

The temperatures were measured with a Leeds and Northrup platinum resistance thermometer fitted with compensating leads, the resistances being determined with a Callendar bridge. The thermometer was calibrated at +100, 0 and —95.5". the melting point of toluene, and was later checked against the freezing point of a pure sample of normal heptane which had been previously determined with a calibrated thermocouple. The end of the thermometer was placed inside the hollow ring of the cell and, in every case, the temperature was held constant to within 0.1" for ten or fifteen minutes before making a measurement. At least two capacity readings differing from one another by less than 0.03% were made at each temperature in order to eliminate any possibility of error due to temperature variation. Densities were measured with a pycnometer (Fig. 2) somewhat similar in form to that used by Isnardi.[4] The bulb, A, which had a volume of about 25 cc., was connected to the stoppered overflow bulb B by the carefully ground joint C. The vessel was filled and hung with the bulb A immersed in the bath. When the liquid in the pycnometer had had time to attain the temperature of the bath, the bulb B was removed and the level of the liquid adjusted to a definite height in the capillary D. The bulb B was then replaced and the pycnometer removed from the bath, allowed to come to room temperature and weighed. Deposition of frost on the cold pycnometer was prevented by immersion in ether while it was warming up. The usual corrections were made in weighing and calibration was effected at different temperatures with toluene and with water. By proper design and grinding of the joints pycnometers were obtained which, when filled with hexane at −90°, tightly stoppered and allowed to come to room temperature, lost only 5 to 10 milligrams in weight on standing for fifteen hours. The probable error in the low temperature density determinations was 0.1% but in the measurements carried out at ordinary temperatures it was not more than 0.03%. The probable error in the dielectric constant measurements was 0.2%, although the relative accuracy within a given series of measurements was usually greater than this.

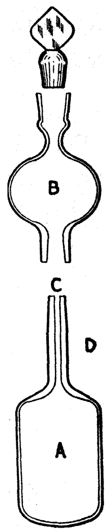

Fig. 2.—Pycnometer.

Preparation of Materials

Chlorobenzene was prepared in the manner described in the first paper. Pure normal hexane was obtained from the Eastman Kodak Company and treated just as was the petroleum hexane in the earlier investigation. Its refractive index at 20° for sodium light was found to be 1.37527, agreeing within the experimental error with the value 1.37536 given in Landolt-Bornstein "Tabellen" (5th ed.).

Ethyl bromide was freshly prepared from alcohol and potassium bromide, shaken once with concentrated sulfuric acid, then several times with water, dried over fused calcium chloride and distilled. Its density, d_4^{20} = 1.452, differed from the values found in the literature. It was

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[4] Isnardi, Z. *Physik*, 9,153 (1922).

washed again three times with small quantities of concentrated sulfuric acid, seven times with ice water and dried over fused calcium chloride. It all distilled at 38.5° and had a density, d_4^{20} = 1.4586. This value agrees with those given in Landolt-Börnstein "Tabellen," 1.4555 and 1.4569, but differs greatly from the value d_4^{20} = 1.430 given in "International Critical Tables." The density measurement has been repeated on other samples of ethyl bromide and the value d_4^{20} = 1.458 is believed to be correct.

Chloroform was shaken several times with concentrated sulfuric acid, with dilute sodium hydroxide and with water. It was dried over anhydrous potassium carbonate and fractionated.

Results

The dielectric constants and densities of hexane, ethyl bromide, chloroform, chlorobenzene and solutions of the substances in hexane were measured over the entire range of temperatures at which the materials were liquid under atmospheric pressure. The data were plotted against temperature on a very large scale and the values at 10° temperature intervals read off. The values for different mixtures at the same temperature were then plotted against c_2, the mole fraction of the polar substance, ethyl bromide, chloroform or chlorobenzene, as the case might be, and the

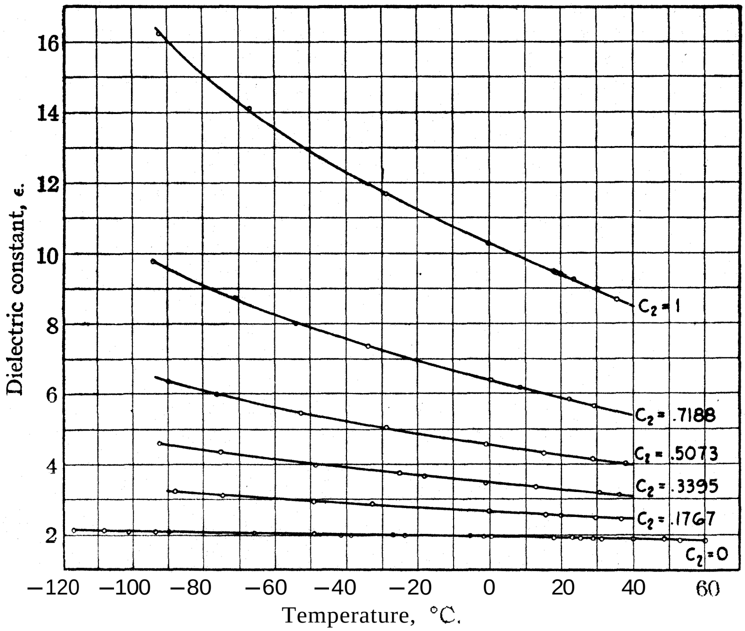

Fig. 3.—Temperature variation of dielectric constants of hexane–ethyl bromide mixtures.

values for $c_2 = 0.05$, 0.1, 0.2, 0.3, etc., were read off. By means of the equations $P_{12} = (\epsilon - 1)/(\epsilon + 2)\ (c_1M_1 + c_2M_2)/d$, and $P_2 = [(P_{12} - P_1)/c_2] + P_1$, in which ϵ = the dielectric constant, d = the density, c_1 and c_2 = the mole fractions and M_1 and M_2 = the molecular weights, the molar polarization, P_{12}, of the mixtures, and P_2, the polarization of the polar substance, were obtained at the different concentrations and temperatures. The values of P_2 at one temperature were plotted against c_2 and the curve was extrapolated to $c_2 = 0$ to obtain P_∞, the polarization at infinite dilution, where the molecules should be oriented at random when no external field is applied. A series of curves at different temperatures gave P_∞ over the entire temperature range within which the mixtures were liquid.

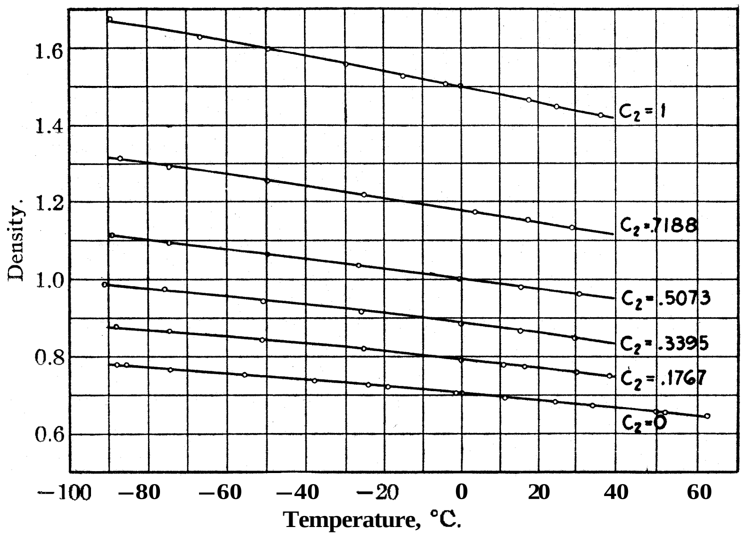

Fig. 4.—Temperature variation of densities of hexane-ethyl bromide mixtures.

Table I contains the values of the dielectric constant, ϵ, and the density, d, at the actual temperatures of measurement, for the pure liquids, but, for the sake of brevity, omits the measurements on the mixtures. Table II gives for each combination of substances the values of ϵ and d interpolated at 10° intervals for each mixture studied, but omits the data interpolated for $c_2 = 0.05$, 0.1, 0.2, etc. The results shown under $c_2 = 0$ in the hexane-ethyl bromide combination are for petroleum hexane which, as in the earlier work, was used in the mixtures. The constants of this mixture of isomers were, of course, somewhat different from those for the pure normal hexane given in Table I. In Table III, the polarization of both the pure normal hexane and the petroleum hexane are designated as P_1, which is assumed to be independent of concentration. For each of the other substances the polarization of the pure liquid, P_2, is shown beside P,, the polarization extrapolated to infinite dilution.

Fig. 3 shows the temperature variation of the dielectric constant of each mixture of petroleum hexane and ethyl bromide, each curve being designated by the value of c_2, the mole fraction of ethyl bromide, and Fig. 4 shows in similar fashion the temperature variation of the densities.

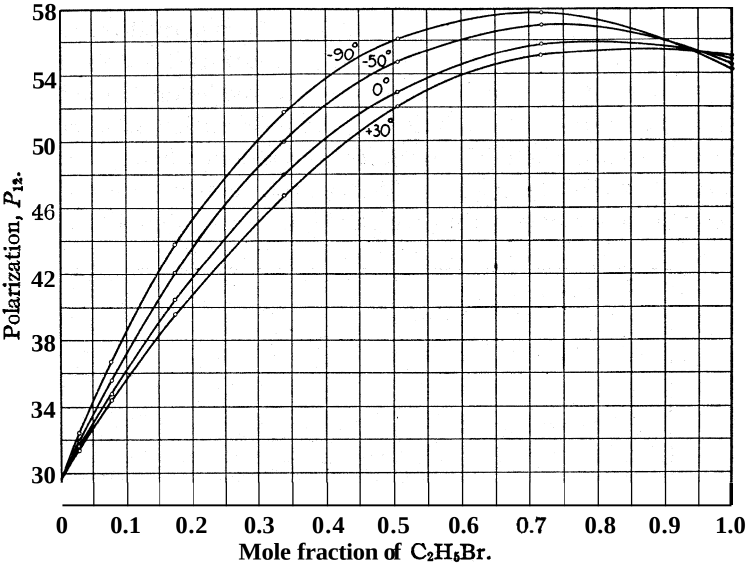

Fig. 5.—Molar polarizations of hexane–ethyl bromide mixtures.

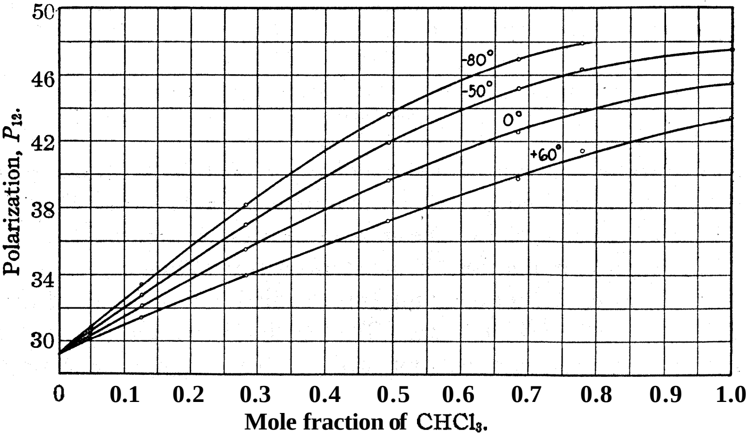

Fig. 6.—Molar polarizations of hexane–chloroform mixtures.

The curves for the mixtures of the other substances which are not shown are similar to these in form. Figs. 5, 6 and 7 show the variation with concentration of the molar polarization of the mixture, P_{12}, at a given temperature. For each set of mixtures curves are given at convenient intervals over the entire temperature range. It is hoped that the variation of P_2 with temperature and concentration may be treated in a later paper.

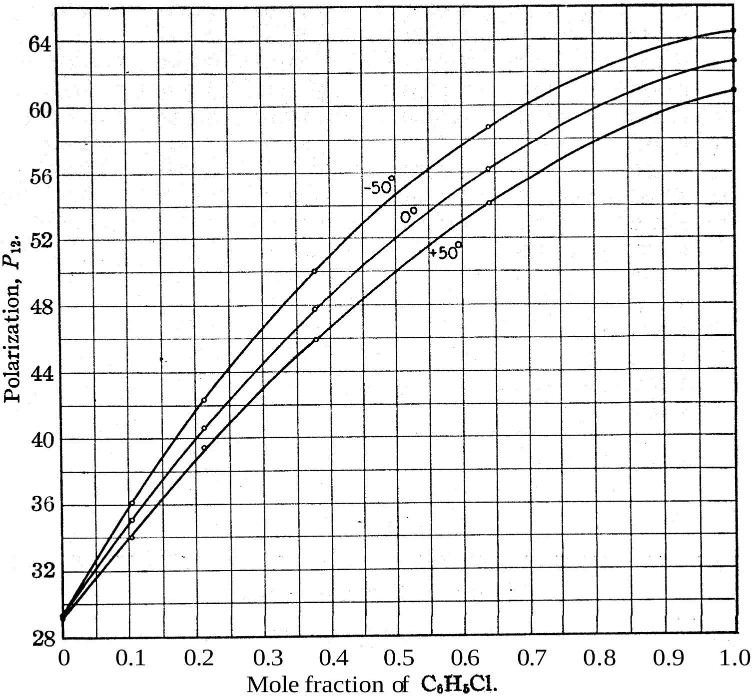

Fig. 7.—Molar polarizations of hexane–chlorobenzene mixtures.

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF PURE LIQUIDS

n-Hexane				Ethyl Bromide			
t, °C.	ϵ	*t*, °C.	*d*	*t*, °C.	ϵ	*t*, °C.	*d*
−91.3	2.051	−89.5	0.7540	−92.3	16.22	−89.2	1.6737
−89.4	2.050	−77.6	.7442	−66.7	14.10	−66.4	1.6283
−71.6	2.023	−63.6	.7324	−28.6	11.67	−49.0	1.5950
−61.3	2.006	−47.0	.7185	0	10.28	−29.5	1.5572
−57.8	2 003	−29.5	.7035	+18.3	9.49	−14.6	1.5274
−37.0	1.976	−12.7	.6886	+18.5	9.48	− 3.3	1.5050
−19.3	1.948	− 1.3	.6787	+18.7	9.45	0	1.4996
− 0.1	1.918	+10.4	.6686	+20.0	9.40	+17.7	1.4634
+ 9.1	1.907	+15.8	.6664	+23.8	9.25	+25.2	1.4479
+15.0	1.898	+27.5	.6555	+30.3	8.99	+36.6	1.4245
+28.2	1.879	+38.3	.6458	+35.5	8.67		
+39.4	1.863	+50.1	.6325				
+47.1	1.848	+61.2	.6219				
+57.0	1.824	+67.0	.6158				

TABLE I *(Concluded)*

Chloroform				Chlorobenzene			
t, °C.	ε	t, °C.	d	t, °C.	ε	t, °C.	d
−62.6	6.810	−61.3	1.6397	−49.0	7.240	−42.7	1.1742
−61.0	6.748	−54.6	1.6271	−45.5	7.150	−24.5	1.1561
−59.7	6.707	−48.7	1.6161	−25.8	6.684	− 3.3	1.1314
−55.6	6.576	−25.0	1.5725	+ 0.1	6.013	0	1.1277
−51.8	6.428	−23.4	1.5696	+18.3	5.662	+18.7	1.1080
−49.6	6.387	− 1.1	1.5282	+22.0	5.593	+46.3	1.0777
−40.5	6.120	0	1.5265	+23.2	5.580	+73.5	1.0475
−22.4	5.703	+24.2	1.4814	+29.2	5.475	+97.2	1.0206
−18.8	5.552	+50.1	1.4308	+47.8	5.174	+103.3	1.0319
−15.0	5.466	+59.8	1.4116	+75.1	4.822	+124.5	0.9914
− 2.2	5.195			+100.0	4.516	+126.0	.9906
+ 4.5	5.078			+100.5	4.460		
+17.2	4.825			+115.5	4.346		
+18.7	4.802			+126.0	4.174		
+35.5	4.520						
+45.8	4.351						
+54.0	4.231						
+58.6	4.163						

TABLE II

INTERPOLATED VALUES OF DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS

HEXANE–ETHYL BROMIDE

Mole fraction of C_2H_5Br = t, °C.	0	0.0309	0.0783	0.1767	0.3395	0.5073	0.7188	1.000
	Dielectric Constant							
−90	2078	2.270	2.568	3.240	4.573	6.360	9.60	16.05
−80	2 063	2.245	2.520	3.152	4.416	6 095	9.12	15.15
−70	2048	2219	2.476	3.075	4.270	5.856	8.68	14.35
−60	2.033	2.194	2.437	3.002	4.135	5.634	8.28	13.62
−50	2.017	2.170	2.400	2.934	4.006	5.418	7.91	12.95
−40	2.002	2.147	2.365	2.870	3.887	5.217	7.56	1232
−30	1.987	2.123	2.331	2.808	3.776	5.027	7.23	11.75
−20	1.972	2.101	2.300	2.752	3.667	4852	6.93	11.22
−10	1.957	2.080	2.270	2.700	3.570	4.690	665	10.73
0	1.942	2.059	2.240	2648	3.476	4.544	6.38	10.27
+10	1.927	2038	2.211	2.599	3.385	4.407	6.14	9.82
+20	1.912	2.018	2.181	2.552	3.294	4 275	5.91	9 41
+30	1.896	1.997	2.153	2.500	3.200	4.146	5.65	898
+40	1.880	1.975	2.124	2.444	3.112	3.985	5.40	8.44
+50	1.862	1.953	2.093					
+60	1.843	1.929						
	Density							
−90	0.7813	0.7973	0.8235	0.8804	0.9880	1.1155	1.3176	1.6752
−80	.7734	.7887	.8140	.8704	.9767	1.1026	1.3020	1.6555
−70	.7650	.7800	.8048	.8605	.9653	1.0897	1.2867	1.6358
−60	.7564	.7710	.7956	.8505	.9540	1.0768	1.2717	1.6162
−50	.7478	.7622	.7862	.8405	.9423	1.0640	1.2560	1.5966
−40	.7390	.7533	,7770	.8305	.9306	1.0512	1,2405	1.5776

TABLE II (*Continued*)

Mole fraction of C_2H_5Br = t, °C.	0	0.0309	0.0783	0.1767	0.3395	0.5073	0.7188	1.000
	Density							
−30	.7300	.7443	.7677	.8206	.9193	1.0383	1.2255	1.5580
−20	.7210	.7356	.7585	.8106	.9078	1.0256	1.2100	1.5384
−10	.7120	.7266	.7493	.8005	.8963	1.0126	1.1947	1.5188
0	.7032	.7174	.7400	.7906	.8848	1.0000	1.1797	1.4993
+10	.6940	.7082	.7302	.7800	.8735	0.9872	1.1640	1.4790
+20	.6854	.6990	.7204	.7693	.8615	.9743	1.1480	1.4586
+30	.6760	.6897	.7103	.7588	.8495	.9616	1.1313	1.4380
+40	.6668	.6800	.7003	.7480	.8374	.9486	1.1144	1.4164
+50	.6574	.6702	.6900					
+60	.6473	.6600						

HEXANE–CHLOROFORM

Mole fraction of $CHCl_3$ = t, °C.	0.0517	0.1277	0.2862	0.4953	0.6856	0.7803	1.000
	Dielectric Constant						
−90	2.201	2.409	....	....	....	....	
−80	2.177	2.371	2.848	3.710	4.785	5.465	
−70	2.155	2.335	2.786	3.584	4.582	5.210	....
−60	2.133	2.302	2.726	3.469	4.400	4.984	6.720
−50	2.113	2.271	2.668	3.363	4.234	4.778	6.402
−40	2.092	2.241	2.612	3.265	4.076	4.586	6.100
−30	2.072	2.212	2.560	3.174	3.934	4.406	5.825
−20	2.053	2.186	2.512	3.090	3.802	4.256	5.580
−10	2.033	2.159	2.466	3.010	3.680	4.108	5.356
0	2.014	2.134	2.426	2.937	3.568	3.972	5.150
+10	1.995	2.109	2.387	2.867	3.462	3.843	4.960
+20	1.976	2.086	2.348	2.800	3.360	3.720	4.783
+30	1.957	2.062	2.310	2.736	3.266	3.606	4.614
+40	1.938	2.038	2.270	2.670	3.173	3.496	4.450
+50	1.919	2.012	2.230	2.606	3.076	3.394	4.292
+60	1.900	1.984	2.189	2.544	2.974	3.295	4.140
	Density						
−90	0.8122	0.8580	....	....	....	....	
−80	.8032	.8484	0.9547	1.1175	1.2955	1.3967	....
−70	.7942	.8388	.9440	1.1053	1.2810	1.3813	1.6560
−60	.7853	.8295	.9333	1.0933	1.2668	1.3660	1.6374
−50	.7763	.8198	.9225	1.0804	1.2525	1.3500	1.6188
−40	.7673	.8102	.9120	1.0685	1.2380	1.3342	1.6000
−30	.7582	.8008	.9008	1.0560	1.2234	1.3188	1.5814
−20	.7488	.7914	.8900	1.0435	1.2087	1.3034	1.5633
−10	.7392	.7818	.8790	1.0303	1.1963	1.2875	1.5445
0	.7304	.7722	.8682	1.0173	1.1800	1.2706	1.5262
+10	.7210	.7623	.8576	1.0042	1.1648	1.2557	1.5080
+20	.7116	.7522	.8462	0.9914	1.1498	1.2398	1.4895
+30	.7013	.7420	.8353	.9784	1.1342	1.2236	1.4704
+40	.6922	.7317	.8236	.9652	1.1188	1.2073	1.4516
+50	.6823	.7214	.8116	.9517	1.1038	1.1905	1.4315
+60	.6721	.7115	.7998	.9380	1.0888	1.1737	1.4105

TABLE II (*Concluded*)

HEXANE–CHLOROBENZENE

Mole fraction of C_6H_5Cl = t, °C.	0.1068	0.2132	0 3798	0.6458	1.000
	Dielectric Constant				
−80	2.532	3.053	....	....	....
−70	2.490	2.977	3.848	5.484	....
−60	2.448	2.908	3.730	5.268	....
−50	2.409	2.844	3.620	5.086	7.28
−40	2.371	2.784	3.518	4.882	7.01
−30	2.336	2.728	3.424	4.717	6.758
−20	2.304	2.677	3.336	4.560	6.502
−10	2.273	2.629	3.257	4.415	6.260
0	2.244	2.584	3.180	4.280	6.027
+10	2.214	2.540	3.108	4.156	5.818
+20	2.184	2.497	3.040	4.038	5.633
+30	2.153	2.456	2.977	3.928	5.460
+40	2.120	2.416	2.913	3.827	5.300
+50	2.084	2.377	2.846	3.723	5.150
+60	2.050	2.347	2.777	3.627	5.016
+70		2.300	2.706	3.538	4.888
+80				3.443	
	Density				
−80	0.8140	0.8548	....	....	....
−70	.8050	.8460	0.9166	1.0325	....
−60	.7960	.8368	.9067	1.0225	....
−50	.7868	.8278	.8967	1.0120	1.1838
−40	.7777	.8188	.8868	1.0015	1.1726
−30	.7687	.8096	.8774	0.9914	1.1614
−20	.7597	.8005	.8677	.9810	1.1502
−10	.7505	.7912	.8578	.9704	1.1394
0	.7414	.7815	.8480	.9603	1.1280
+10	.7323	.7723	.8384	.9500	1.1172
+20	.7232	.7632	.8285	.9398	1.1060
+30	.7138	.7532	.8185	.9296	1.0953
+40	.7044	.7434	.8086	.9192	1.0840
+50	.695	.7333	.7983	.9087	1.0732
+60	.685	.7228	.7878	.8980	1.0620
+70		.7124	.7770	.8872	1.0513
+80				.8760	

TABLE III

POLARIZATIONS

t, °C.	C_6H_{14} Petroleum	normal	C_2H_5Br		$CHCl_3$		C_6H_5Cl	
	P_1	P_1	P_2	P_∞	P_2	P_∞	P_2	P_∞
−90	29.15	29.57	54.24	143.5	...	..	...	...
−80	29.15	29.63	54.32	138.5	...	62.1	...	106.5
−70	29.15	29.65	54.38	135.0	...	60.2	...	103.0
−60	29.16	29.66	54.47	131.0	47.85	58.9	...	100.0
−50	29.16	29.69	54.54	127.0	47.42	57.5	64.33	97.0
−40	29.16	29.72	54.60	123.5	46.97	56.0	64.00	94.0
−30	29.20	29.72	54.67	118.5	46.53	54.6	63.70	91.0

TABLE III (*Concluded*)

t, °C.	C_6H_{14} Petroleum P_1	C_6H_{14} normal P_1	C_2H_5Br P_2	C_2H_5Br P_∞	$CHCl_3$ P_2	$CHCl_3$ P_∞	C_6H_5Cl P_2	C_6H_5Cl P_∞
−20	29.23	29.76	54.74	114.3	46.14	53.1	63.30	89.3
−10	29.23	29.79	54.84	111.0	45.76	52.3	62.88	87.5
0	29.26	29.81	54.92	107.9	45.42	51.1	62.47	85.5
+10	29.28	29.87	54.98	105.5	45.04	50.0	62.06	83.5
+20	29.29	29.92	55.07	103.3	44.70	49.7	61.74	81.5
+30	29.30	29.91	55.07	100.2	44.35	48.8	61.40	79.0
+40	29.28	29.90	54.82	97.6	44.02	48.3	61.12	77.8
+50	29.23	29.85		95.4	43.63	47.5	60.82	76.8
+60	29.16	29.74			43.30	47.3	60.65	76.0
+70							60.40	

Discussion of Results

The values for petroleum hexane are slightly different from those for the pure normal hexane, but their polarizations are so nearly equal and show such similarity of behavior that the use of the petroleum hexane as an indifferent solvent is justified. In Fig. 3 the almost horizontal curve for $c_2 = 0$ shows the small temperature variation of the dielectric constant of petroleum hexane, but a rapid increase of slope accompanies increase in the ethyl bromide content of the mixture. The density curves, on the other hand, are nearly parallel.

As was observed in the earlier work, the curves in which the values of P_{12}, the polarizations of the mixtures, are plotted against the concentration of the polar substances, show strong deviation from the theoretical linearity, the deviation, as before, being larger, the larger the moment of the polar molecule, the greater the concentration of the polar molecules and the lower the temperature. Thus, the P_{12} curves for chloroform, which has the smallest moment of the three polar substances studied, are nearly straight lines in the dilute region, and the curve for 60° shows only a small departure from linearity throughout its course, but this departure from linearity increases as the temperature is lowered. Chlorobenzene, which has a larger moment, shows a noticeable curvature throughout all the curves, but the curvature increases with decreasing temperature and increasing concentration. The effect upon one another of the dipoles in the ethyl bromide molecules, which have the largest moments of the three considered, is so great that the curves pass through a maximum. As this effect diminishes rapidly with rising temperature, the curves intersect almost at one point, the polarization of the mixture containing 0.95 mole fraction of ethyl bromide being practically independent of temperature. In pure ethyl bromide increasing thermal agitation by increasing the freedom of the molecules from one another's fields does more to facilitate the orientation of the molecule in an externally applied field than it does to destroy this orientation by the increasing violence of the motion. Thus, the polarization actually increases with rising temperature instead of decreasing as required by the Debye equation, $P = a + b/T$, which should apply when the molecules are free to assume a random orientation. In terms of the quantities discussed in the earlier work, the constant

$a = P_E + P_A$, $b/T = P_M$, and the constant $b = 4\pi N\mu^2/9k$, where
P_E = the polarization due to electronic shifts induced in the molecules
P_A = the polarization due to shifts of atoms or radicals induced in the molecules
P_M = the polarization due to orientation of the dipoles
μ = the electric moment of a single molecule
N = the number of molecules in a gram molecule = 6.061×10^{23}, and
k = the molecular gas constant = 1.372×10^{-16}

As it is apparent that the polarization should be a linear function of $1/T$, the values of both P_2 and P_∞ are plotted against $1/T$ in Fig. 8. All the curves are linear, but the P_2 curve for ethyl bromide gives a negative value of b and the P_2 curves for the other two substances give values of b much lower than those which determine the slopes of the P, curves. The low values of b are due to the orienting effects of the dipoles upon one another, which cause the deviation from linearity of the $P_{1,2} - c_2$ curves. The values of P, , to which the Debye equation should apply, vary so much with temperature that the linearity of these curves affords strong evidence in support of the Debye theory.

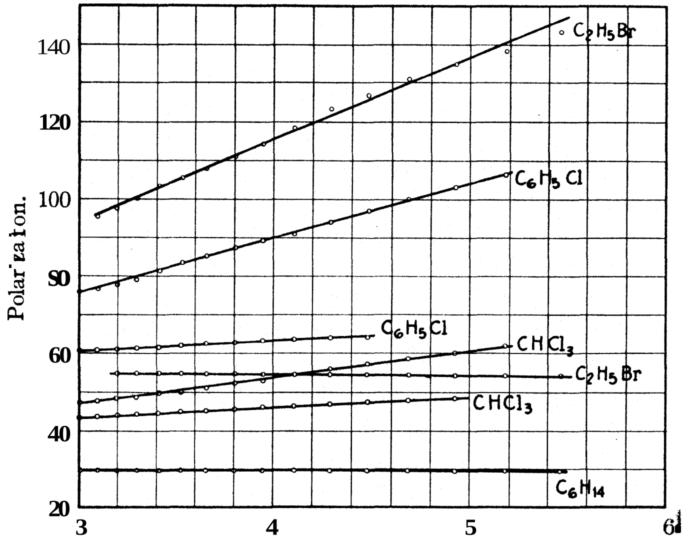

Fig. 8.—Variation of P_2 and P_∞ with $1/T$. (The higher curve for each substance represents P_∞.)

If the equation is written in the form $PT = aT + b$ and the values of PT are plotted as ordinates against T, as abscissas, we should obtain a straight line of which the slope is *a* and the ordinate at 7' = 0 is b. In

Fig. 9, $P_\infty T$ is plotted for the three polar substances and P_1T for hexane. The values obtained from these curves for a, b and μ, calculated from b, are given in Table IV, together with the values of $MR_\infty = P_E$, calculated by extrapolation of refractive index data from the visible region, and values of P_A, calculated from the relation $P_E + P_A = a$.

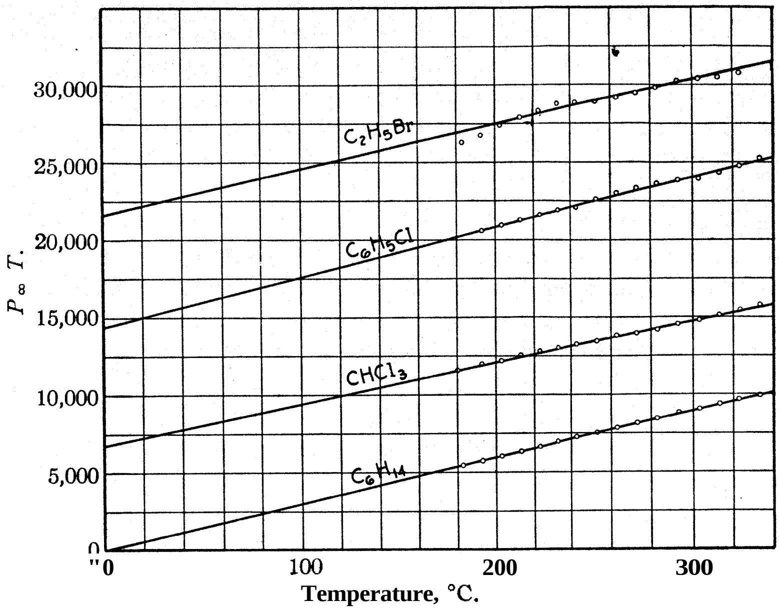

Fig. 9.—Variation of $P_\infty T$ with T.

TABLE IV

VALUES OF FUNDAMENTAL CONSTANTS

	a	P_E	P_A	b	$\mu \times 10^{18}$
C_6H_{14}	29.8	29.20	0.6	0	0
$CHCl_3$	26.6	20.84	5.8	6800	1.05
C_6H_5Cl	33.2	29.93	3.3	14150	1.52
C_2H_5Br	29.5	18.55	(11)	21420	1.86

The very small difference between a and P_E for hexane confirms the value of 0 obtained from the fact that b = 0. The value of $\mu = 1.05 \times 10^{-18}$ for chloroform differs from the value 0.95×10^{-18} obtained by Sänger[5] from measurements on the vapor by an amount no greater than that which might arise from the probable errors of the two determinations. This agreement between results in the liquid and in the gaseous states provides further confirmation of the Debye theory. The values for ethyl bromide are less satisfactory than those for the other substances, as the great variation of P_2 with c_2 in the dilute region makes difficult the extrapolation to $c_2 = 0$

[5] Sänger, *Physik. Z.*, **27**, 556 (1926).

thereby causing some inaccuracy in P_∞ and in the results derived from the P_∞ curves. As a very small variation in the drawing of the P_∞ T–T curves causes a considerable variation in the values of a, the values obtained for P_A cannot be regarded as exact although the value 5.8 for chloroform agrees with the difference, 6.0, between P_E and the polarization of the solid in the tabulation of Ebert.[6] a and P_A for ethyl bromide are probably too high as a result of the difficulties which have been discussed. The values of the moments agree roughly with those calculated by one of the authors[7] by a very approximate method from data on the pure liquids: $\mu \times 10^{18}$ for C_6H_{14}, 0; $CHCl_3$, 1.25; C_6H_5Cl, 1.42; C_2H_5Br, 1.56. In view of the necessary disregard of P_A and the impossibility of taking accurate account of the orienting effects of the molecules upon one another in these old calculations, the agreement of their results with the accurate values of the present work is better than would be expected.

In conclusion, it may be stated that a new, though somewhat inaccurate, method has been employed to obtain the value of P_A, the polarization due to the shifts of atoms and groups of atoms within the molecule, that accurate values have been obtained for the electric moments of molecules by measuring not merely the concentration variation but also the temperature variation of the dielectric constants and densities of liquid mixtures, and that the validity of the Debye equation as applied to liquids at infinite dilution has been established.

Summary

The dielectric constants of solutions of ethyl bromide, chloroform and chlorobenzene in hexane have been measured with a capacity bridge over the entire range of temperature and concentration within which the mixtures are liquid and the densities have been determined with a special form of pycnometer.

The polarizations calculated from these data have been used to estimate approximate values for the polarization due to the shifts of atoms and groups of atoms within the molecule, to obtain accurate values for the electric moments of the molecules and to establish the validity of the Debye equation as applied to infinitely dilute liquids.

As in earlier work, it is found that the molecules affect one another more strongly, the greater their moments, the greater their concentrations and the lower the temperature.

PRINCETON, NEW JERSEY

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[6] Ebert, *Z. physik. Chem.*, 113, 1 (1924).

[7] Smyth, THIS JOURNAL, 46, 2151 (1924).

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BAROPHORESIS IN GELS

BY HARRY SOBOTKA AND ALBERT B. SABIN

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During an investigation dealing with the diffusibility of certain bacteriological solutions through semi-solid media, which was undertaken by one of the authors (A. B. S.) together with Professor J. Klostermann, some fundamental points had to be elucidated. The diffusion of solutions into gels does not lend itself to as precise and simple experimentation as the diffusion of gases into one another. The influence of concentration and temperature, as well as of the nature of the solute, had to be studied. A remarkable influence of the direction of diffusion upon its rate was observed in these experiments: this phenomenon will be dealt with in the third section of this paper; its influence has already been taken into consideration in the preceding sections.

I

As the progress of colored solutions in gelatinous media may readily be followed, the distance and not the quantity diffused through the gel in a definite time was determined. This distance was measured from the vertex of the interface to the point within the gel where the slightest trace of the diffusing solution could still be visibly detected. "d," distance, could be determined, for example, for bromo cresol purple or sodium dichromate with an accuracy of ±1 mm., whereas for methylene blue it could be measured with a precision of $\pm {}^1/_4$ mm.

For diffusion in gels[1] where secondary disturbances by "convection currents" are apparently avoided, Auerbach[2] has shown experimentally that the amount diffused since the beginning of the experiment is proportional to the distance between the interface and a point within the gel at which the concentration of the diffusing substance is a definite fraction, for example, one-tenth of its concentration in the original solution. When diffusion is measured by the distance between interface and limit of detectable diffusion, as indicated before, this distance is found proportional to the square root of time.[3] The limit of detectability must correspond to a definite concentration of the dye; assume this concentration to be 10^{-8} and the concentration of the supernatant solution to be 0.1% or 10^{-3}. Then "d" may be termed $l_{1/10,000}$ in analogy to Auerbach's $l_{1/10}$ or $l_{1/100}$ designating the distance between the interface and the point where 1/10 or

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[1] Voigtlander, Z. *physik. Chem.*, 3,316 (1889).

[2] Auerbach, *Kolloid* Z., 35,202 (1924); 37, 379 (1925).

[3] (a) Stefan, *Sitzber. Wiener Akad. Wiss.*, 79, 215 (1879); (b) Chabry, J. *phys.*, [2] 7, 115 (1888); (c) *Z. physik. Chem.*, 2, 440 (1888).

1/100 the concentration of the supernatant solution prevails. Thus d can be expected to be proportional to the total amount diffused. This holds true since the distance of diffusion was experimentally found proportional to the square root of time and the square root of time is in turn proportional to the amount diffused as derived by Pick's law[4] and actually observed by Voigtlander.[1]

In our experiments diffusion followed the equation

$$d = k\sqrt{t} \qquad (1)$$

d is conveniently expressed in millimeters and t in hours from the beginning of the experiment.

k of equation (1) was found to be practically constant within the limits of error in the estimation of d under the condition of our experiments.[5]

k can be used as an index for the rate of diffusion for a given system and was thus employed for comparative purposes where this rate was involved.

Diffusion of methylene blue presents a different appearance from that of bromo cresol purple, picric acid or sodium dichromate. In the case of methylene blue the agar gel is deeply stained and the limit of diffusion is sharply demarcated. Beyond this zone of deeply stained gel there is another zone of lighter shade which in turn can be differentiated from the unstained agar. As long as the supernatant solution of methylene blue is not exhausted, this "fading zone" is narrower than or equal to 0.5 mm. in width at room temperature and 2.5 mm. at 37°. The dye is adsorbed up to the point of saturation of the agar and the progress of saturation is the controlling factor in the speed of methylene blue diffusion in its early stages. Since no unlimited supply of methylene blue was used it was exhausted before the entire agar column was stained.

With solutions of dichromate, picric acid or bromo cresol purple—substances which are not adsorbed by the agar—equilibrium is established when the concentration is uniform throughout the entire agar column and the supernatant. The diffusion of these substances is not hindered by adsorption; thus their progress in the gel is about three times faster than that of methylene blue (see Fig. 1 and Table I) and the limit of perceptible diffusion is not sharply demarcated.

With methylene blue, after equilibrium is practically reached, the further progress of diffusion is controlled by the establishment of secondary equilibria between stained and unstained agar. At this point the "fading zone" grows considerably wider and by the further diffusion of methylene blue

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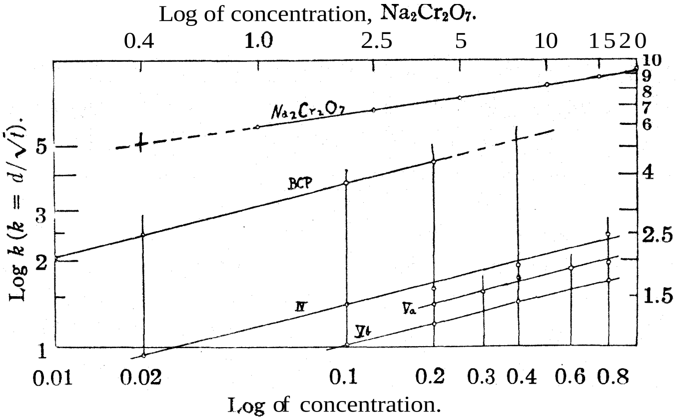
[4] Fick, *Pogg. Ann.*, 94, 59 (1855).

[5] When, as in the case of methylene blue, the experiment had to be extended over a period of many days the k's of the lower concentrations slightly decreased (see Table IV). Lower k's invariably obtained at the beginning of diffusion, as also observed by other workers, are usually explained by the greater proportional error in the determination of *d*.

new zones of diminishing concentration are developed. After a 0.1% solution has been diffusing for three weeks, two distinct zones besides the fading zone could be differentiated, the ratio being 5:2:1 at room temperature and 4:2:2 at 37°; the first figure corresponds to the darkest band, the second to the following one and the third to the extent of the fading zone.[6]

When a drop of melted agar was spread on a slide to form a film and by means of a capillary tube a round hole was scooped from the center and filled with methylene blue solution, two distinct concentric zones of deep and lighter color and a third exterior "fading" ring were observed under the microscope.



BCP = bromo cresol purple; IV, Va, Vb = methylene blue, for details see tables. Notice the use of different abscissas in the case of $Na_2Cr_2O_7$.

Fig. 1.—Relation between concentration and diffusion.

II

The influence of the concentration of the diffusing substance on its diffusion can be expressed by the mathematical relation between the quotients of two concentrations and of the two corresponding constants, k.[7]

Table I

Average Values for $k = d/\sqrt{t}$ for Various Substances and Concentrations

All experiments except No. 4 at 22°. Numbers of experiments refer to Tables where complete data are given.

		Concentration, %													
No.	Subs.	0.01	0.02	0.1	0.2	0.3	0.4	0.6	0.8	1.0	2.5	5.0	10.0	15.0	20.0
4	Methylene blue (37°)	..	0.96	1.41	1.56	..	1.90	..	2.45	..	..	..	..	..	..
5a	Methylene blue	..	..	..	1.36	1.57	1.75	1.83	1.91	..	..	..	..	..	..
5b	Methylene blue	..	..	1.02	1.18	..	1.45	..	1.68	..	..	..	..	..	..
—	Bromo cresol purple	2.04	2.47	3.72	4.39	..	6.22[a]	..	..	..	..	..	..	..	..
—	$Na_2Cr_2O_7$	..	..	..	..	..	5.07[a]	..	..	5.91	6.56	7.19	8.25	8.84	9.25

[a] Values extrapolated from equation (4).

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[6] Traube and Kohler, *Intern. Z. physik. chem. Biol.*, 2, 205 (1915).

[7] Auerbach's (see ref. 2) $l_{1/10}$ and $l_{1/100}$ is independent of the concentration.

When plotting the logarithms of the concentrations as abscissas and the values of log k as ordinates, approximately straight lines were obtained. Thus the quotient of two k's in an experiment should be a definite power of the quotient of the two concentrations.

$$\left(\frac{c_1}{c_2}\right)^n = \frac{k_1}{k_2} \tag{2}$$

The power n was calculated for all possible combinations in each experiment according to

$$\frac{\log k_2 - \log k_1}{\log c_2 - \log c_1} = n \tag{3}$$

n was found with methylene blue between 0.02% and 0.8 to be: 0.249 ± 0.050 (Expt. 4); 0.241 ± 0.076 (Expt. 5a); 0.246 ± 0.024 (Expt. 5b); for bromo cresol purple (0.01–0.2%), 0.255 + 0.008; and for sodium dichromate (1–20%), 0.157 ± 0.023. When $n' = 2n$ is calculated from

$$\frac{k_1^2}{k_2^2} \text{ or } \frac{d_1^2/t}{d_2^2/t} = \left(\frac{c_1}{c_2}\right)^{n'} \tag{4}$$

it is approximately $^1/_2$ for methylene blue and bromo cresol purple and $^1/_3$ for sodium dichromate; thus k^2 is proportional to the square root of the concentration in the former and to the cube root in the latter.

The influence of the concentration on the diffusion is the same at 5, 22 and 37°, as can be seen from Table II where the diffusion of 5 and 15% sodium dichromate is compared at these temperatures. The influence of the temperature is in turn independent of the concentration.

TABLE II

MUTUAL INFLUENCE OF TEMPERATURE AND CONCENTRATION UPON DIFFUSION OF SODIUM DICHROMATE IN AGAR-AGAR

Each value for $k = d/\sqrt{t}$, as given in this table, is the average of 5 observations on 12 test-tubes.

	Values for $k_{t,c}$			Quotients		
	$t = 5°$	$t = 22°$	$t = 37°$	$\frac{k_{22,c}}{k_{5,c}}$	$\frac{k_{37,c}}{k_{5,c}}$	$\frac{k_{37,c}}{k_{22,c}}$
$c = 5\%$	6.06	8.06	8.88	1.33	1.47	1.10
$c = 15\%$	7.22	9.64	10.52	1.33	1.46	1.09
Quotient $\frac{k_{t,15}}{k_{t,5}}$	1.19	1.19	1.18	..	..	..

Influence of Temperature.—Both in 5 and 15% solutions, dichromate was found to diffuse 1.33 times faster at 22° than at 5° and 1.10 times faster at 37° than at 22°. The figure 1.10 for the interval 22–37° is remarkably lower than the analogous figure for methylene blue, as recorded in Table III and Fig. 2; the diffusion of methylene blue at 37° is proceeding at doubled speed compared with 22°.[8] This may be explained by the fact that agar adsorbs the methylene blue and thus impedes its diffusion; with increasing

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[8] The experiments 4 and 5a, b of Table I cannot be compared with regard to temperature since different gels were used.

temperature, however, adsorption is diminished and diffusion may increase.

Table III

Influence of Temperature on Diffusion of Methylene Blue

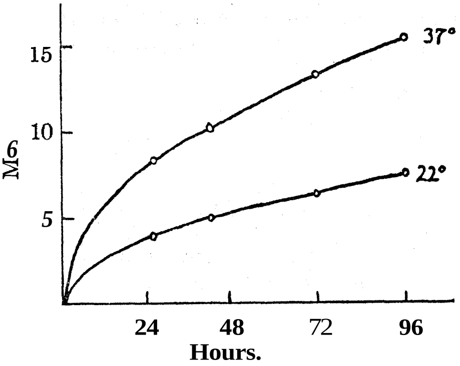
Each figure is the average of 5 similar tubes. "U" means mouth of tube upward; "I" tube inverted (c = 0.1%).

Position of tubes	Temp., °C.	Distance d in millimeters after 26 hours	43 hours	72 hours	96 hours
U	37	7.5	8.7	12.3	15.4
U	22	3.8	4.2	5.9	7.6
I	37	9.1	11.5	14.3	15.4
I	22	4.0	5.8	7.0	7.7

III

Peskoff[9] observed that potassium permanganate in small concentration contained in a ferrihydroxide sol will diffuse faster into a supernatant layer of urea solution than into a layer of distilled water. He termed this and similar phenomena "barophoresis;" it is due to the greater specific gravity of the urea solution as compared with the lesser sp. gr. of the lower layer in so far as only the diffusible permanganate is considered. His observations were confined to sols.

Concerning the diffusion in gels Freundlich[10] states that "the motion of the dissolved substance takes place by diffusion alone; convection is almost entirely absent, since the molecules of the solvent as elementary parts of the adsorption envelope and in the amicronic capillaries have to a great extent lost their free mobility." Liesegang[11] asserts even more positively that "diffusion in jellies is free from those convection disturbances which are hardly to be avoided in liquids." Ruhland[12] in his diffusion experiments placed test-tubes half filled with the gel mouth downward into the colored solution; thus he intended to exclude what he thought might be the accelerating effect of gravity, but he does not offer any observation of such influences when omitting this precaution.



Values are averages of those given for "U" and "I" in Table III.

Fig. 2.—Influence of temperature on diffusion of methylene blue.

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[9] Peskoff, *Kolloid-Z.*, 33, 215 (1924).

[10] Freundlich, "Colloid and Capillary Chemistry," Methuen and Co., London, 1926, p. 729.

[11] Liesegang in Alexander, "Colloid Chemistry," Vol. I, Chemical Catalog Co., New York, 1926, p. 783.

[12] Ruhland, *Jahrb. f. wissensch. Botanik*, *51*, *376*, 402 (1912).

We shall now describe the phenomenon of barophoresis in gels. The suspicion that the direction of diffusion might affect its rate was justified when considerable differences between diffusion in the direction of gravity and against it were actually observed. To several tubes containing "nutrient agar"[13] a few cc. of a 0.2% solution of methylene blue was added, the tubes were covered with vaseline and half of them were turned mouth downward, After twenty-four hours the dye had diffused farther in the inverted than in the other tubes.

If any variation in the rate of diffusion with direction were to be expected at all it would be in favor of faster diffusion in the direction of gravity. To account for the paradoxical phenomenon it was assumed that the density of the intermicellular liquid in the agar might be greater than that of the diffusing solution, thus establishing convection currents.

TABLE IV

DIFFUSION OF METHYLENE BLUE INTO A 2% AGAR GEL AT 37°

Every figure represents the average value for three test-tubes; U = test-tubes with mouth turned upward, I = inverted, H = horizontal.

Concn., %	Dir.	Diffusion in mm. and k = $d/\sqrt{t}$ after t hours t = 12	39	63	87	129	158	229	277	Av. for k	$k_I - k_U$
0.02	U	d2.8	4.3	7.0	8.2	8.8	9.3	10.7	...	0.79	+0.29
		k0.80	0.69	0.89	0.88	0.77	0.74	0.71	...	±0.06	
	1	d3.66	...	10.0	10.5	12.0	12.7	15.0	...	1.08	
		k1.05	...	1.27	1.13	1.05	1.00	1.00	...	±0.06	
	H	d3.33	4.8	9.7	10.2	11.5	11.5	13.8	...	0.99	
		k0.95	0.77	1.23	1.10	1.00	0.91	0.91	...	±0.09	
0.1	U	d5.0	7.2	12.5	13.0	15.6	15.6	21.0	...	1.37	+0.07
		k1.43	1.16	1.58	1.40	1.37	1.24	1.39	...	±0.09	
	I	d4.6	7.2	13.7	14.5	16.3	17.5	22.5	...	1.44	
		k1.31	1.16	1.73	1.56	1.43	1.39	1.49	...	±0.13	
	H	d5.33	8.4	14.5	15.3	17.8	19.0	22.5	...	1.56	
		k 1.52	1.35	1.83	1.65	1.56	1.51	1.49	...	±0.10	
0.2	U	d6.0	9.5	14.2	15.5	18.0	19.3	22.0	23.2	1.59	−0.11
		k1.71	1.63	1 8	1.67	1.58	1.53	1.46	1.40	±0.10	
	I	d5.0	8.7	13.5	15.0	17.2	18.5	20.7	22.5	1.48	
		k1.43	1.40	1.71	1.60	1.51	1.47	1.37	1.35	±0.09	
	H	d6.16	10.0	14.7	15.7	18.3	19.3	22.5	23.5	1.62	
		k1.76	1.61	1.86	1.69	1.61	1.53	1.49	1.42	±0.10	
0.4	U	d7.16	12.0	17.5	19.3	22.0	23.5	27.5	29.0	1.96	−0.20
		k2.05	1.94	2.22	2.07	1.93	1.87	1.82	1.75	±0.12	
	I	d5.5	10.0	16.0	17.7	20.7	22.0	26.0	28.0	1.76	
		k1.57	1.61	2.02	1.90	1.82	1.75	1.72	1.70	±0.11	
	H	d7.5	12.2	17.3	19.7	22.3	23.8	27.8	29.3	1.99	
		k2.14	1.96	2.20	2.12	1.96	1.89	1.84	1.80	±0.12	
0.8	U	d9.16	15.2	23.2	25.2	29.0	31.6	36.6	38.8	2.57	− 0.24
		k2.62	2.45	2.94	2.71	2.54	2.50	2.42	2.34	±0.15	
	I	d7.66	13.4	20.7	22.7	27.2	29.2	34.0	37.5	2.33	
		k2.19	2.16	2.62	2.44	2.39	2.32	2.25	2.25	±0.09	
	H	d8.88	14.3	21.5	23.8	28.0	30.0	35.8	37.5	2.45	
		k2.64	2.31	2.72	2.56	2.46	2.38	2.37	2.25	±0.12	

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[13] 1.5% agar, 0.3% beef extract, 1.0% peptone and 0.5% NaCl.

TABLE V

DIFFUSION OF METHYLENE BLUE (a) INTO A 2% AGAR GEL CONTAINING 0.2% SODIUM CHLORIDE; (b) INTO "NUTRIENT AGAR" AT 22°

For U and I see Table IV. Each k given in this table is the average from four tubes,

Concn. of methylene blue, %	(a) Agar plus 0.2% NaCl k_I	k_U	$k_I - k_U$	(b) Nutrient agar k_I	k_U	$k_I - k_U$
0.1	....	....	....	1.13 ± 0.06	0.92 ± 0.04	+0.21
.2	1.51 ± 0.01	1.23 ± 0.02	+0.27	1.30 ± 0.04	1.07 ± 0.05	+0.23
.3	1.68 ± 0.05	1.47 ± 0.02	+0.21	....	....	....
.4	1.72 ± 0.04	1.79 ± 0.05	−0.07	1.59 ± 0.04	1.30 ± 0.04	+0.29
.6	1.77 ± 0.02	1.89 ± 0.07	−0.12	....	....	....
.8	1.83 ± 0.01	2.00 ± 0.02	−0.17	1.77 ± 0.04	1.59 ± 0.02	+0.18

In order to test this assumption the densities of both the diffusing solution and the intermicellular fluid had to be varied. The "nutrient agar" was replaced by a plain agar gel. Up to a methylene blue concentration of 0.1%, the same effect was observed as with nutrient agar; above 0.1% diffusion in the inverted tubes was slower than in the upright ones. When using a 2% agar containing 0.2% sodium chloride, the "critical concentration" of the methylene blue was raised to 0.4%, which is higher than in plain agar, but lower than in nutrient agar. Even a concentration as high as 0.8% failed to reverse the effect with nutrient agar, where the diffusion was invariably ahead in the inverted tubes with 0.8% as well as with the lower concentrations.

The diffusion of sodium dichromate in the concentrations used is so much faster that any accelerating effect due to convection currents in the intermicellular fluid, if present, is below the range of detectability. With bromo cresol purple, too, the acceleration is but very slight; none the less and despite the lesser accuracy in the reading, the critical concentration of this dye toward plain agar can be placed approximately at 0.1% in the range of that of methylene blue.

The diffusion of sodium dichromate can only be observed in relatively concentrated solution. A difference in favor of the upright tubes was only observed during the later stages and this can be explained by the fact that in the inverted tubes the layer adjacent to the interface decreases in concentration by the rapid diffusion of the dichromate. Since this exhausted layer, because of its lesser density, does not mix readily with the denser strata below, a lower actual concentration will prevail at the interface. The inhomogeneity of the dichromate solution in inverted tubes is manifested by the stratification taking place when these tubes are moved. In the upright and in horizontal tubes the contact layer is situated beneath or alongside of the rest of the solution and as it becomes exhausted homogeneity is maintained by convection currents in the solution. This effect can be made responsible only for a delay of diffusion in the inverted tubes, but not for an acceleration in these tubes nor for any effect upon upright or horizontal tubes.

Method.—Ten grams of large shreds of agar-agar are thoroughly cleaned by dialysis in a cheese-cloth against running water for twenty-four to forty-eight hours. The agar is heated with 500 cc. of distilled water to make a 2% solution. Portions of 10 cc. each of this melted gel are put into a series of test-tubes of uniform diameter. If the gel in the tubes is not covered within four to five hours after it has set, it is remelted and allowed to cool for an hour to insure an even meniscus and to prevent leakage between the shrinking agar and the glass. Each tube receives 3 cc. of whatever solution is used in the experiment and a layer of vaseline is put on top to prevent evaporation and to render possible the inversion of the tubes; "d" may conveniently be measured by means of a compass.

IV

The density of the intermicellular liquid of a gel cannot be directly determined and indirect methods for its estimation had to be resorted to. At first a definite amount of agar gel was extracted with a definite amount of distilled water for several days and the density of this extract determined. The density of the intermicellular fluid, however, may be greater than that of the aqueous extract; for not only may the agar form a very dilute saturated solution but it may also contain small amounts of diffusible substances which finally would be equally divided between the gel and the extract, provided that they are not adsorbed by the gel. For this reason the amount of dissolved and diffusible substances in the gel had to be determined.

Diffusible substances, for example, electrolytes, present to a limited amount per unit weight of agar and dissolved in the intermicellular fluid, will cause varying density of the extract depending on the volume of water used. The agar itself or any slightly soluble substance forming a considerable portion of it will on extraction yield a saturated solution and the density of the extract should be independent from the volume used, since increasing amounts of water will dissolve additional amounts. Whether or not both these factors are present and in what proportion was determined by the following method.

Three series of several test-tubes were set up (a) with 8 cc. of 2% agar gel, prepared as previously described, and 8 cc. of sterile distilled water above the gel; (b) with 4 cc. of agar and 12 cc. of distilled water and (c) with 2 cc. of agar and 14 cc. of distilled water. All these tubes were covered with sterile vaseline and kept at room temperature. The total solids in the filtered supernatants were determined after the intervals recorded in Table VI.[14]

The amount of extractible and diffusible material per cc. of extract should be equal to that contained in 1 cc. of the intermicellular fluid after equilibrium is attained. Let x equal the amount of diffusible material in 1 cc. of the original agar gel and y the amount of agar or of a slightly soluble portion of the agar dissolved in 1 cc. Then at equilibrium each tube

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[14] These experiments were carried out under sterile conditions to exclude interference by bacterial contamination. Also, controls showed neither the glass tubes nor the vaseline contained extractible matter nor the distilled water any ponderable residue.

will contain dissolved in series (a) $8x + 16y$, in series (b) $4x + 16y$ and in series (c) $2x + 16y$. One cc. of series (a), (b) and (c) will contain:

$$A = x/2 + y \qquad (5)$$
$$B = x/4 + y \qquad (6)$$
$$C = x/8 + y \qquad (7)$$

Hence the values for x and y can be computed

$$x = \frac{8}{3}(A - C) \qquad x = 4(A - B) \qquad x = 8(B - C) \qquad (8)\ (9)\ (10)$$

$$y = \frac{1}{3}(4C - A) \qquad y = 2B - A \qquad y = 2C - B \qquad (11)\ (12)\ (13)$$

The introduction of a third independent equation (three series) permits of checking x and y by computation from these three pairs of equations.

TABLE VI

EXTRACTION OF TWO TYPES OF SOLUBLE MATTER FROM 2% AGAR-AGAR GEL

The table gives mg. per cc.; the total solids were actually determined in samples of 20 or 10 cc.

		First experiment		Second experiment 6 days	
	Series	2 days	4½ days	"U"	"I"
Total solids,	(a)	0.66	0.80	0.77	1.06
mg. per cc.	(b)	.40	.58	.545	.655
	(c)	.365	.50	.47	.525
Values for	(8)	.81	.80	.80	1.425
x from	(9)	1.04	.88	.90	1.62
equation	(10)	.28	.64	.60	1.04
x (average)			.77	.77	1.36
Values for	(11)	.23	.40	.37	.35
y from	(12)	.14	.36	.32	.25
equation	(13)	.33	.42	.395	.395
y (average)			.39	.36	.33
$x + y$			1.16	1.13	1.69

Consistent values for x and y were obtained after four and one-half days, as shown by the first experiment in Table VI; y reached constant values by this time ranging around 0.35 mg. per cc. When inverting the tubes the diffusion and extraction of x from within the agar column was enhanced. Further increases of x when extraction was prolonged over weeks cannot be due to matter originally present in free solution. To show the probable identity of the extracted substance, or its portion y, with agar, a little water was added to dried extracts (for example, those recorded in the next paragraph); the dry material swelled, dissolved upon heating, and after cooling the solution set into a gel.

The bearing of these results upon constitutional problems of agar-agar will be made the subject of a separate investigation. For our present scope it is safe to assume that the sum $x + y$ found after five days represents a maximum for the dissolved matter in the intermicellular fluid. The average of the three values for $x + y$ given in Table VI is $(1.16 + 1.13 + 1.69)/3 = 1.33$ mg. per cc.

The relation between specific gravity and total solids can be derived from experiments like these.

One hundred and twenty-three cc. of mixed extracts from the above experiments had a specific gravity of 1.000185 and contained 42.6 mg. of solid matter, that is, 0.345 mg. per cc. when dried at 100°.

Ten cc. of agar spread over one side wall of a square bottle was covered with 115 cc. of water in a horizontal position. The resulting extract, of specific gravity = 1.00021, contained 4.3 mg. per 10 cc. The latter figure incidentally yields, from $x = 12.5\ (0.43 - y)$, $x = 0.87$ mg. per cc., when assuming $y = 0.36$ mg., in good agreement with the previous results.

The density of the undiluted intermicellular fluid containing three to four times more total solids than these extracts should range near 1.0006 and 1.0007.

Assuming that the increment of density of such dilute solutions can be evaluated by simple addition, the intermicellular fluid in agar containing 0.2% of sodium chloride should be near 1.002 (from 1.00145 for aqueous 0.2% of sodium chloride solution plus the above estimation for plain agar).

For "nutrient agar" the density of a six-day extract, using 25 cc. of distilled water above 50 cc. of nutrient agar, was 1.0044. The dissolved matter belongs for the most part to the readily soluble group "x." Thus the increment of density for the intermicellular fluid must be at least $0.0044 = (50 + 25)/(50)$; thus specific gravity $\geq$ 1.0066.

The specific gravities of methylene blue and bromo cresol purple solutions,

TABLE VII

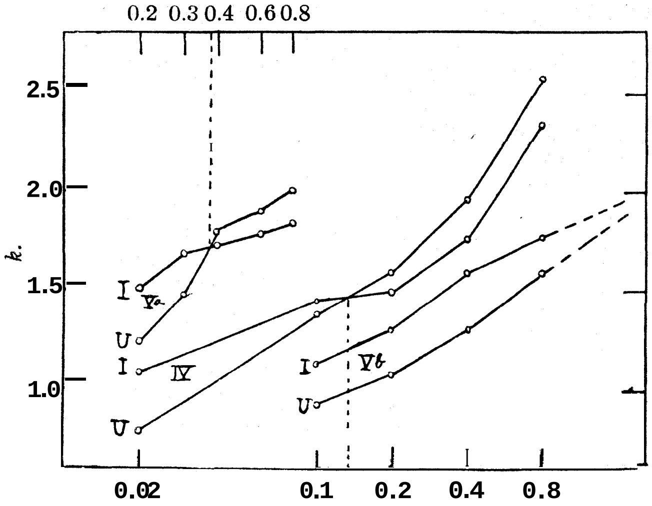
SPECIFIC GRAVITIES OF DIFFUSING SOLUTIONS AND INTERMICELLULAR FLUIDS

Values $d_{22°}^{22°}$ **for diffusing solutions pycnometrically, for intermicellular fluids indirectly**

Methylene blue	$d_{22°}^{22°}$	**Nutrient agar**
0.8	1.00297	>1.0066
.4	1.00148	
.2	1.00070	0.2% **NaCl agar**
.1	1.00037	1.0020
.02	1. 0 m	
.01	1.00003	
Bromo Cresol Purple		**Plain 2% agat**
.2	1.00108	1.0006–
.1	1.00057	1 0007
.02	1.00011	
.01	1.00006	
$Na_2Cr_2O_7$		
1.0	1.007	
20.0	1.141	

used in the diffusion experiments, were determined pycnometrically and compared with those of the intermicellular fluids in Table VII.

This comparison reveals that the "critical concentration" of methylene blue for nutrient agar is far above 0.8%; for 0.2% sodium chloride agar near 0.5% and for plain agar below 0.2%. Graphical extrapolation and intrapolation of the experiments recorded in Tables IV–V yields empirical "critical concentrations" of nearly 2% for nutrient agar, a little below 0.4% for sodium chloride agar and 0.15% for plain agar, in good accordance with the above deductions.



Concentration of methylene blue.

U = **upright, I = inverted test-tubes. IV plain agar; Va (for clearness' sake these two curves are moved to the left, as indicated by values for abscissas in left upper corner, ordinates are the same as for the other four curves) agar containing 0.2 % of NaCl; Vb nutrient agar.**

Fig. 3.—Influence of direction upon rate of diffusion.

Although a more satisfactory explanation for the influence of gravity upon diffusion in gels is hard to conceive, we ought to mention the observation that diffusion in horizontal tubes proceeded as fast as or even faster than in those tubes that were the faster ones among the two vertical directions. (Table IV, series "H"). This corroborates the explanation of the phenomenon by convection currents in the intermicellular fluid, since swift convection will take place across a vertical plane between two liquids differing in specific gravity.

Summary

1. Various methods of measuring diffusion in semi-solid media lead to identical conclusions, both experimentally and theoretically. Two types

of diffusion of colored solutions into gels, with and without adsorption, are described. The rate of diffusion follows a simple mathematical law.

2. The rate of diffusion is a simple function of the concentration of the solution. The influence of temperature upon both types of diffusion is discussed.

3. Considerable differences between the rates of diffusion in upward and in downward direction can be observed under certain conditions. The application of the term "barophoresis" is suggested for this phenomenon. For a given system consisting of a gel and a diffusing substance, a critical concentration of the latter is found at which the sense of barophoresis is reversed.

4. The specific gravities of the intermicellular fluids of various gels are indirectly determined. They coincide with the specific gravities of the corresponding critical concentrations.

NEW YORK, N. Y.

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

SOLUBILITY OF LEAD MONOXIDE AND BASIC LEAD CARBONATE IN ALKALINE SOLUTIONS

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Heretofore no attempt has been made to prepare a comprehensive table of the free energies of formation of the compounds of the metallic elements. From a cursory search of the literature it was seen that data were available from which the free energies of formation of a large number of compounds of lead could be calculated. These values are particularly interesting because of the technical importance of lead, its amphoteric character and its marked tendency to form "basic" compounds. We have therefore undertaken a systematic investigation of the free energy of the lead compounds. The new equilibria measured are those between the basic carbonate, the hydrated monoxide, the red and yellow monoxides and the plumbite ion. The results of these measurements will be given in the present paper.

Berl and Austerweil[1] measured the solubility in sodium hydroxide solutions of lead monoxide prepared by heating pure basic lead carbonate. Their results appeared untrustworthy since the value of the solubility in pure water was much higher than that obtained by other investigators. Their oxide was evidently neither the most stable form[2] nor the most important. Only the dissolved lead was determined, and the amount of sodium hydroxide in the solutions was calculated according to assumptions which we shall show to be erroneous.

[1] Berl and Austerweil, Z. *Elektrochem.*, 13, 165 (1907).

[2] A discussion of the allotropy of lead monoxides will be given in a later paper.

Glasstone[3] measured the solubility of the red form in sodium hydroxide solutions of varying concentration and found the solubility, in normal solutions, only slightly different from that of the yellow form. The measurements with normal solutions were carried out at room temperature. The liquid was gently stirred over the surface of the solid, without disturbing the latter, by means of a current of air free from carbon dioxide. In the series of determinations using the red form, solutions which were considered supersaturated were merely placed in contact with the solid phase, without stirring, in a thermostat at 25°. He concluded that the two forms were identical, and attributed his observed differences[4] to a variation in the size of the particles. Applebey and Reid[6] repeated the measurements in normal solutions. They used carefully prepared oxides and qualitatively confirmed the measurements of Ruer[6] who had found different solubilities for the two forms in water. Berl and Austerweil[1] have also shown that in hydroxide solutions below one molal or thereabouts, the lead monoxide forms the monoplumbite ion in accordance with the reaction

$$\mathrm{PbO(s)} + \mathrm{KOH(aq)} = \mathrm{KHPbO_2(aq)} \qquad (1)$$

but from their data it was impossible to evaluate accurately the constant of the reaction, and it was decided to redetermine the solubility of the red and yellow forms of the monoxide.

Rubenbauer,[7] Wood[8] and Glasstone[9] determined the solubilities of the hydrated lead monoxide at 18 and 25°. These investigators assumed the concentration of the sodium hydroxide in the final solution to be that of the original solution, less the concentration of the lead hydroxide dissolved in excess of its solubility in water. Rubenbauer and Wood shook their mixtures continuously but only for short periods. Apparently equilibrium was not attained in any case, as our experiments show concentrations of lead about 50% higher. Because of the uncertainty respecting the composition of the solid phase and the lack of sufficient analytical data, these experiments have been repeated.

The solubility of the basic lead carbonate,[10] in potassium hydroxide solutions was also studied. This is a condensed system of four components two phases and therefore three degrees of freedom. Starting with carbon

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[3] Glasstone, J. *Chem. Soc.*, 119,1689 (1921).

[4] Larger differences were obtained in shaking experiments, but these were not considered equilibrium values.

[5] Applebey and Reid, J. *Chem. Soc.*, 121,2129 (1922).

[6] Ruer, *Z. anorg. Chem.*, 50, 265 (1906).

[7] Rubenbauer, *Z. anorg. Chem.*, 30,336 (1902).

[8] Wood, *J. Chem. Soc.*, 97, *884* (1910).

[9] Glasstone, *J. Chem. Soc.*, 121, 58 (1921).

[10] The individuality of the basic lead carbonate, $\mathrm{Pb_3(CO_3)_2(OH)_2}$, has been established by the work of Pleissner, *Arb. kais. Gesundh.*, 26, 384 (1907).

dioxide free solutions only one degree remains if the temperature is fixed, and the analysis for total alkalinity and lead is sufficient to determine the system. The equilibrium involved may be represented by

$$Pb_3(CO_3)_2(OH)_2(s) + 7KOH(aq) = 3KHPbO_2(aq) + 2K_2CO_3(aq) + 3H_2O(l) \quad (2)$$

Preparation of Materials.—The red and yellow forms of lead monoxide were prepared by dehydrating the hydrated monoxides by a modification of the method described by Geuther[11] and by Ruer.[6] At temperatures just below the boiling point the red modification was obtained when the concentration of the hydroxide was about 12 M and the yellow form when it was about 5 M. Hydrated lead monoxide prepared and purified as described below was heated[12] with the sodium hydroxide solution in a flask provided with an air condenser and a soda lime tube to prevent the access of carbon dioxide. The products in each case were of uniform color. The solids were washed by decantation with boiling water a large number of times. They were stored under conductivity water.

The hydrated lead monoxide was prepared according to the method of Pleissner.[10] It was washed thoroughly by decantation with conductivity water. Some of the solid thus obtained was dried to constant weight in a vacuum desiccator over sulfuric acid. On analysis we found 89.8% of lead, compared with 90.39% calculated for $3PbO \cdot H_2O$ and 89.22% calculated for $2PbO \cdot H_2O$.[13] This was considered satisfactory owing to the difficulty of removing the last traces of water. The composition of this hydrated lead monoxide is to be further discussed in a later paper.

The basic lead carbonate was prepared by the method of Auerbach and Pick.[14] Lead sulfate was shaken with successive portions of dilute sodium carbonate solutions. It was washed and stored as were the above solids. Analyses for lead were made on samples dried in a vacuum desiccator. The agreement between the values found, 80.0, 80.9 and 80.8% of lead and 80.13 % calculated from the formula was considered quite satisfactory.

Procedure.—Samples of the solid phases, usually between 15 and 25 g., were transferred with some of the water under which they were kept to long-necked, round-bottomed flasks kept free from air by a slow stream of nitrogen. This precaution was not taken in a few experiments, but the results did not differ appreciably. The solids were then washed several times with portions of the solution with which they were to be shaken. Finally, the flask was filled almost to the neck and the end of the neck sealed off.

The flasks were rotated in a thermostat at 25 * 0.05°, according to the method described by Randall and Vietti.[15] When the equilibrium was to be approached from

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[11] Geuther, Ann., 219, 56 (1883).

[12] This method is similar to the one employed by Applebey and Reid.

[13] Müller, *Z. physik. Chem.*, 114, 129 (1924), found 89.75 % of Pb.

[14] Auerbach and Pick, Arb. *kais.* Gesundh., 45, 113 (1913).

[15] Randall and Vietti, THIS JOURNAL, 50, 1526 (1928).

supersaturation, the flasks were first shaken for several weeks in a thermostat at 32°, the shaker of which was governed by an eccentric rod and gave a jerking vertical motion to the flasks. The period of rotation varied from one week to several months. In general, four to six weeks were allowed for the attainment of equilibria in experiments which were to be considered final.

Analysis of Liquid Phase.—The method of sampling was similar to that described by Randall and Vietti.[15] The total alkalinity was determined by weight titrations using methyl orange as an indicator. Standardized hydrochloric acid solution was added in slight excess and final adjustment to the first appearance of orange from the yellow side was made by alternate additions of hydrochloric acid and sodium hydroxide. The lead was first precipitated as the hydrated oxide but the precipitate dissolved completely before the end-point was reached. The hydroxide was neutralized and the carbonate in the solutions from basic carbonate was changed to carbon dioxide.

Lead was determined by the precipitation of lead chromate. The neutralized solutions were heated to boiling and transferred to Pyrex beakers. Each flask was rinsed first with boiling water to which a few drops of glacial acetic acid had been added, then with two small portions of boiling water. A few cc. of 1 M sodium acetate were added. After the solution had been heated to boiling, the addition of potassium chromate was made a little at a time. Gentle boiling was continued until the precipitate had taken on a shade of orange and settled completely, leaving a clear solution. The precipitate was collected and washed on Gooch crucibles which had been alternately washed and dried to constant weight. The oven used was kept at 135°.

Analysis of the Solid Phase.—The solid phase left after sampling was transferred along with some of the equilibrium solution to a weighed beaker and immediately weighed. The beakers were then put in a vacuum desiccator and were dried to constant weight. From the loss of weight the amount of water and thence the amount of dissolved salts and other solutes associated with it were calculated. The solid was analyzed for lead, corrections being made for the solutes from the liquid phase.

The Equilibrium Constants.—As a first approximation, we may assume that the total lead in the equilibrium solution is in the form of $HPbO_2^-$ and that this is completely converted to Pb^{++} in the titration

$$HPbO_2^- + 3H^+ = 2H_2O + Pb^{++} \qquad (3)$$

Three moles of hydrochloric acid are thus used to change each mole of dissolved lead. Since in the solutions from the basic carbonate equilibria (Equation 2) the concentration of the carbonate ion is two-thirds that of the dissolved lead, the number of moles of hydrochloric acid required to decompose the carbonate ion is four-thirds the number of moles of dissolved lead present. The total amount of hydrochloric acid used, less the sum of the amounts necessary to change $HPbO_2^-$ to Pb^{++} and CO_3^{--} to H_2CO_3, gives the approximate concentration of the hydroxide ion. All concentrations are given in moles per 1000 g. of water and vacuum corrections are used throughout.

While the principle of the ionic strength as enunciated by Lewis and Randall[16] has not been experimentally studied in the case of these compounds we may as an approximation assume that the activity coefficient of a given

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[16] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, pp. **373, 380** and **382.**

salt is the same in all solutions of the same ionic strength. Since the potassium ion does not take part in the reactions, no further error is introduced by utilizing the principle of the independent activity coefficient of the ions. We shall assume that the activity coefficient of HPbO_2^- is the same as that of NO_3^-, and use the preliminary revised values of the activity coefficients which are now being compiled in this Laboratory. We shall find that the values of the equilibrium constants on these assumptions vary somewhat with the ionic strength, owing to experimental errors and to the fact that the above assumptions are not exact. These differences become smaller at the lower ionic strengths.

As a first approximation we may assume the ionic strength to be given by the following equation,

$$\mu = m'(\text{KOH}) + m'(\text{KHPbO}_2) + 3m'(\text{K}_2\text{CO}_3) \qquad (4)$$

where values of $m'(\text{KOH})$, etc., are the approximate molalities obtained as above and we shall find that the values of the ionic strength thus calculated are the same as the final value.

The assumption that the lead is converted completely to lead ion in the titration is justified by the following considerations. Pleissner[10] measured the conductivity of solutions of the hydrated lead monoxide at 18° and found 4 X 10^{-5} for the first dissociation constant as a base and approximately 2×10^{-9} for complete dissociation. Using the dissociation constant of water, $K_{291} = 0.58$ X $10\ ^{14}$, we have

$$\text{Pb(OH)}_2 + \text{H}^+ = \text{PbOH}^{\text{C}} + \text{H}_2\text{O};\ K_{291} = 6.9 \text{ X } 10^9 \qquad (5)$$

$$\text{PbOH}^+ = \text{Pb}^{++} + \text{OH}^-;\ K_{291} = 5 \times 10^{-5} \qquad (6)$$

At the end-point in the methyl orange titration the hydrogen-ion concentration is approximately 10^{-4}. Therefore $m(\text{PbOH}^+) = 2 \text{ X } 10\ ^6 m(\text{Pb}^{++})$ and $m(\text{Pb(OH)}_2) = 3 \times 10^{-12} m(\text{Pb}^{+}+)$.

We may now consider the distribution of the dissolved lead in the equilibrium solutions among its possible forms. Berl and Austerweil[1] have shown the dissociation constant of lead hydroxide as a monobasic acid to be about 10^{-12}. In a later paper we shall find

$$\text{Pb(OH)}_2\text{(aq)} = \text{H}^+ + \text{HPbO}_2^-;\ K_{298} = a(\text{H}^+) \times a(\text{HPbO}_2^-)/a(\text{Pb(OH)}_2) = 1.2 \times 10^{-12} \qquad (7)$$

or, combining with the dissociation constant of water

$$\text{Pb(OH)}_2\text{(aq)} + \text{OH}- = \text{HPbO}_2^- + \text{H}_2\text{O};\ K_{298} = a(\text{HPbO}_2^-)/\,a(\text{Pb(OH)}_2) \text{ X } a(\text{OH}^-) = 120 \qquad (8)$$

Taking the activity of the dissolved lead hydroxide equal to its molality, we find

$$m(\text{Pb(OH)}_2) = my\ (\text{HPbO}_2^-)/120m\ \gamma\ (\text{OH}^-) \qquad (9)$$

In a similar way the ratio $m(\text{PbOH}^+)/m(\text{HPbO}_2^-)$ was calculated from the above ratio and the first dissociation of lead hydroxide as a base. In this calculation it was assumed that $a(\text{PbOH}^+) = m(\text{PbOH}^+)$. Thus

$$m(\text{PbOH}^+) = m\gamma(\text{HPbO}_2^-) \times 4 \times 10^{-5}/120m^2\,\gamma^2(\text{OH}^-) \qquad (10)$$

The sum of the molalities of the three forms of dissolved lead is equal to the total molality obtained by analysis.

$$Pb = m(HPbO_2^-) + m(Pb(OH)_2) + m(PbOH^+) \qquad (11)$$

Using values of $m'(OH-)$ obtained as a first approximation and Equations 9, 10 and 11, preliminary values of $m(HPbO_2^-)$, $m(Pb(OH)_2)$ and $m(PbOH+)$ were calculated.

Since the hydroxide ion concentration used in the above calculation might have been too low, the distribution among the various forms of lead so obtained would not be exact. Therefore we make a third approximation in which the hydroxide ion concentration used is calculated from the total alkalinity and the values of $m(HPbO_2^-)$, $m(Pb(OH)_2)$ and $m(PbOH^+)$ found above and $m(CO_3^{--})$ when the basic lead carbonate solutions are considered. Even in the solutions of lowest hydroxide concentration, where values of $m(PbOH^+)$ should be the greatest, they were found to be negligible (of the order $10^{-6}M$) and were therefore neglected. The third approximation yielded values of $m(OH^-)$ which did not differ from the values found by the second approximation, and values of $m(HPbO_2^-)$ and $m(Pb(OH)_2)$ which differed only slightly from those of the second approximation.

The results of the measurements with red lead monoxide are given in Table I. In the first column the letter U indicates that equilibrium was approached from undersaturation, and the letter S from supersaturation.

TABLE I

SOLUBILITY OF RED LEAD MONOXIDE (TETRAGONAL) IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°. $PbO \text{ (red)} + OH^- = HPbO_2^-$

No of expt.	Days of rotation	0.5023 M HCl to 1 g. of soln., g.	$PbCrO_4$ to 1 g. of soln., g.	Pb in solid phase, %	$m'(OH^-)$ 1st approx.	$m'(HPbO_2^-)$ 1st approx.
1U	28	0.1100	0.0008085	92.8	0.04665	0.002516
25"	20	.1090	.0008105	...	.04615	.002516
3S[a]	20	.2258	.002077	92.7	.09229	.006468
4U	24	.2222	.001644	92.72	.09448	.005121
5S[a]	38	.2268	.001679	...	.09645	.005231
6U	28	,2176	.001443	...	.09409	.004493
7U	50	.7043	.009157	...	.2687	.02899

No of expt	$\mu^{1/2}$	$-\log \gamma$ (OH^-)	$-\log \gamma$ $(HPbO_2^-)$	$m(OH^-)$ final	$m(HPbO_2^-)$ final	$\log K_m$	$\log K$
1U	0.222	0.0800	0.1311	0.04705	0.002110	−1.3483	−1.3994
2S[a]	.221	.0800	.1311	.04587	.002102	−1.3388	−1.3890
3S[a]	.314	.0980	.1865	.09278	.005933	−1.1942	−1.2827
4U	.316	.0982	.1880	.09490	.004703	−1.3048	−1.3946
5S[a]	.319	.0986	.1895	.09686	.004808	−1.3042	−1.3951
6U	.314	.0980	.1865	.09433	.004125	−1.3592	−1.4477
7U	.546	.110	.325	.2694	.02823	−0.9799	−1.1949

[a] In Expts. 2 and 3 the solutions were rotated for fifteen days at 32° and in Expt. 5, twenty-one days at 32°, and were then transferred to a thermostat at 25° and rotated for the time indicated in Col. 2.

The second column gives the number of days of rotation, the third the number of grams of 0.5023*M* hydrochloric acid required to neutralize one gram of the solution, the fourth the number of grams of lead chromate precipitated from one gram of the solution and the fifth the percentage of lead in the solid phase (PbO; Pb = 92.8%). Columns 6 to 12 give, respectively, the molality of the OH− (first approx.); the molality of $HPbO_2^-$ (1st approx.); $\mu^{1/2}$; the logarithm of the activity coefficient of the OH−, and that of the $HPbO_2^-$; the final value of the molality of the OH−, and that of the $HPbO_2^-$. Column 13 gives the value of log $K_m = \log [m(HPbO_2^-)/m(OH^-)]$, and the last column gives the logarithm of the equilibrium constant, $K_{298} = (HPbO_2^-)/(OH^-)$.

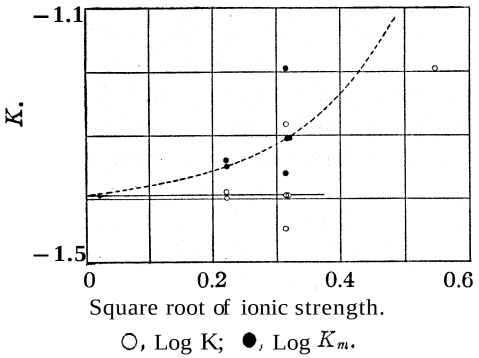


Fig. 1.—Solubility of red lead monoxide in aqueous potassium hydroxide.

The values of log K are plotted as circles in Fig. 1, and those of log K_m as dots. If the assumption that $\gamma (HPbO_2^-) = \gamma (NO_3^-)$ is correct, then the values of log *K* should not change with the ionic strength. If the activity coefficient of potassium hydroxide is the same as that of potassium plumbite, then *K*, should equal *K*. In either case the values should approach the same constant value as the concentration diminishes. The agreement of the results is excellent and we shall choose log $K_{298} = -1.394$, $K = 0.0402$, whence

$$PbO(red) + OH^- = HPbO_2^-; \quad \Delta F^\circ_{298} = 1903 \text{ cal.} \quad (12)$$

The solubility of the yellow form is given in Table II, in which the column headings are the same as those of Table I. The values of log K, and log *K* are plotted in Fig. 2 as in the previous plot.

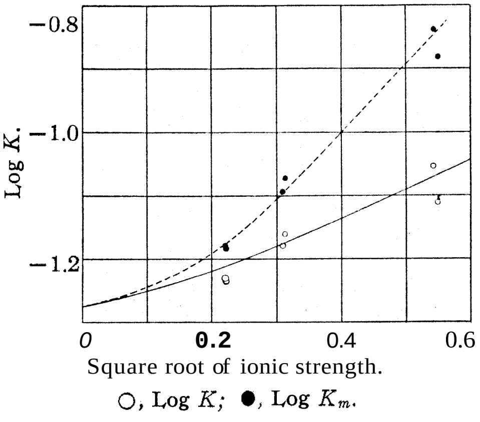


Fig. 2.—Solubility of yellow lead monoxide in aqueous potassium hydroxide.

The results of these measurements are not as satisfactory as those obtained with the red form and we can offer no explanation of the reason why the values of K are not constant. No change in the appearance of

TABLE II

SOLUBILITY OP YELLOW LEAD MONOXIDE: (ORTHORHOMBIC) IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°. $\mathrm{PbO\ (yellow)} + \mathrm{OH^-} = \mathrm{HPbO_2^-}$

No. of expt.	Days of rotation	0.5023 M HCl to 1 g. of soln., g.	$\mathrm{PbCrO_4}$ to 1 g. of soln., g.	Pb in solid phase, %	$m'(\mathrm{OH^-})$ 1st approx.	$m(\mathrm{HPbO_2^-})$ 1st approx.
1U	30	0.1143	0.001134	...	0.04577	0.003522
2S[a]	20	.1130	.001132	92.76	.04515	.003516
3S[a]	20	.2306	.002632	92.7	.08946	.008203
41J	28	.2253	.002483	92.7	,08820	.007738
5U	50	.7247	.01112	...	.2662	.03599
6S	50	.7369	.01207	...	.2560	.03827

No of expt.	$\mu^{1/2}$	$-\log\gamma$ $(\mathrm{OH^-})$	$-\log\gamma$ $(\mathrm{HPbO_2^-})$	$m(\mathrm{OH^-})$ final	$m(\mathrm{HPbO_2^-})$ final	Log K_m	Log K
1U	0.222	0.0802	0.1314	0.04627	0.003031	−1.1838	−1.2349
2S[a]	,221	.0802	.1313	.04565	.003020	−1.1794	−1.2305
3S[a]	.313	.0978	.1840	.09004	.007611	−1.0730	−1.1612
4U	.310	.0975	.1840	.08877	.007171	−1.0927	−1.1792
5U	.550	.1080	.327	.2671	.03503	−0.8823	−1.1013
6S	.543	.1081	.323	.2569	.03725	−0.8387	−1.0536

[a] In Expt. 2 the solution was rotated for fifteen days at 32°; in Expt. 3, seventeen days at 32°, and then transferred to a thermostat at 25° and rotated for the time indicated in Col. 1.

the solid phase was evident, although it is possible that some change may have taken place since a trend in the value of K with changing values of μ is clearly shown. We shall choose the value $\log K_{298} = -1.275$, $K_{298} = 0.0531$, whence

$$\mathrm{PbO(yellow)} + \mathrm{OH^-} = \mathrm{HPbO_2^-};\quad \Delta F^\circ_{298} = 1740\ \text{cal.} \tag{13}$$

The solubility of the hydrated lead monoxide is given in Table III and Fig. 3. The column headings are again the same as those of Table I.

TABLE III

SOLUBILITY OP HYDRATED LEAD MONOXIDE IN POTASSIUM HYDROXIDE: SOLUTIONS AT 25". $\mathrm{PbO\cdot{}^1/_3H_2O(s)} + \mathrm{OH^-} = \mathrm{HPbO_2^-} + {}^1/_3\mathrm{H_2O(1)}$

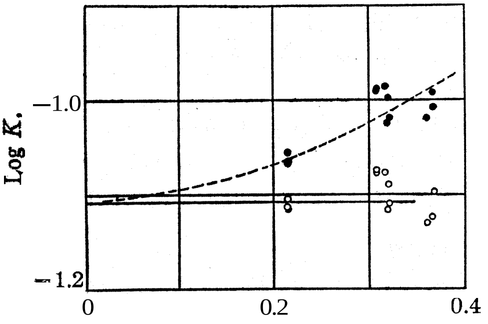
No. of expt	Days of rotation	0 5023 M HCl to 1 g. of soln , g	$\mathrm{PbCrO_4}$ to I g. of soln., g.	Pb in solid phase, %	$m'(\mathrm{OH^-})$ 1st approx.	$m'(\mathrm{HPbO_2^-})$ 1st approx.
IS"	5	0.1115	0.001392		0.04197	0.004323
2S[a]	20	.1115	.001418	87.61	.04174	.004403
3U	30	.1114	.001385	...	.04265	.004301
4S[a]	37	.2305	.003059	85.80	.08543	.009535
5S[a]	21	.2298	.003060	...	.08507	.009538
6U	16	.2408	.003242	85.99	.09022	.01011
7S[a]	26	.2468	.003211	...	.09211	.01001
8U	31	.2472	.003102	85.69	.09411	.009674
9S[a]	30	.2438	.003031	...	.09310	.009451
10U	18	.3098	.003833	85.60	.1177	.01198
11U	33	.3221	.004060	...	.1277	.01269
12S[a]	30	.3195	.003974	...	.1212	.01242

TABLE III *(Concluded)*

No. of expt.	$\mu^{1/2}$	$-\log\gamma$ (OH−)	$-\log\gamma$ ($HPbO_2^-$)	$m(OH^-)$ final	$m(HPbO_2^-)$ final	log K_m	lop K
1S[a]	0.215	0.0784	0.1270	0.04262	0.003672	−1.0647	−1.1133
2S[a]	.215	.0784	.1270	.04242	.003729	−1.0560	−1.1046
3U	.215	.0784	.1270	.04262	.003654	−1.0668	−1.1154
4S[a]	.308	.0971	.1830	.08614	.008815	−0.9900	−1.0759
5S[a]	.308	.0971	.1830	.08579	.008816	−0.9881	−1.0740
6U	.317	.0982	.1885	.09094	.009389	−0.9861	−1.0764
7S[a]	.320	.0989	.1902	.09282	.009314	−0.9985	−1.0898
8U	.321	.0990	,1904	.09398	.009006	−1.0185	−1.1099
9S[a]	,319	.0988	,1900	.09296	.008791	−1.0243	−1.1158
10U	.360	.1034	.2150	.1183	.011324	−1.0189	−1.1305
11U	.367	.1040	.2196	.1224	.01202	−1.0079	−1.1235
12S[a]	.366	.1040	.2190	.1219	.01242	−0.9919	−1 0969

[a] In Expts. 1 and 2 the solutions were shaken for six days at 32°; in Expts. 4 and 5, eighteen days at 32°; in Expt. 7, thirty-seven days at 32°, in Expt. 9, thirty days at 32° and in Expt. 12, twenty-seven days at 32°. The flasks were then transferred to a thermostat at 25° and rotated for the time indicated in Col. 2.

From the analyses of the solid phase after rotation one might assume that the formula of the hydrated lead monoxide was $PbO{\cdot}H_2O$ (85.89%Pb) although the results are irregular. However, some solution is removed with the solid phase, This solution contains potassium hydroxide from which it is difficult to remove the water by desiccation. The appearance of the solid phase does not change and we prefer to consider that the composition of the solid phase in equilibrium with the dilute potassium hydroxide solution is expressed by the formula $3PbO{\cdot}H_2O$ (90.30%-Pb), as was found in the previous section. Referring to Equation 14 we note that this uncertainty affects merely the exponent of the activity of the water in the equilibrium constant, and since the activity of the water in the dilute solutions is nearly unity it does not seriously affect Equation 14. But if we wish to calculate the free energy of formation of hydrated lead monoxide, it is important to choose permanently (even if the choice is quite arbitrary) some one formula. Anomalous results which we were unable to explain were obtained in the case of Expts. 4, 5 and 6. For the most part the results are quite satisfactory and we shall choose log K = log $(HPbO_2^-)(H_2O)/(OH^-) = -1.108$; $K = 0.0780$, whence



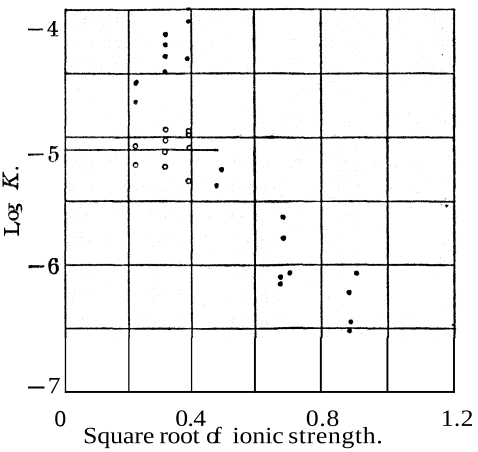
Square root of ionic strength.

○, Log K; ●, Log K_m.

Fig. 3.—Solubility of hydrated lead hydroxide in aqueous potassium hydroxide.

$$PbO\cdot 1/3H_2O(s) + OH^- = HPbO_2^- + 1/3H_2O(1); \Delta F^\circ_{298} = 1512 \text{ cal.} \quad (14)$$

The measurements of the solubility of basic lead carbonate in potassium hydroxide solutions are given in Table IV and Fig. 4. The headings of Cols. 1 to 4 are the same as those of Table I. Col. 5 gives the molality of CO_3^{--}. Cols. 6 to 10 are the same as those of Table I. Cols. 13 to 13 give, respectively, $^1/_4$ the logarithm of the activity coefficient of CO_3^{--}, the final molality of OH^- and the final molality of the $HPbO_2^-$. Col. 14 gives the logarithm of the ratio of molalities $m^3(HPbO_2^-) = m^2(CO_3^{--})/m^7(OH)^-$, and Col. 15 the value of log K. The percentage of lead in the solid phase, in equilibrium in Expt. 4 was 80.08, in Expt. 14 it was 80.21 and in Expt. 17 it was 80.18%, while the percentage of lead corresponding to $Pb_3(CO_3)_2(OH)_2$ is 80.12%.



O, Log K; ●, Log K_m

Fig. 4.—Solubility of basic lead carbonate in aqueous potassium hydroxide.

TABLE IV

SOLUBILITY OF BASIC LEAD CARBONATE IN POTASSIUM HYDROXIDE SOLUTIONS AT 25°

$$Pb_3(CO_3)_2(OH)_2(s) + 7OH^- = 3HPbO_2^- + 2CO_3^{--} + 3H_2O(l)$$

No of rxpt.	Days of rotation	0.5023 *M* HCl to 1 g. of soln., g.	$PbCrO_4$ to 1 g. of soln., g.	$m(CO_3^{--})$ final	$m'(OH^-)$ 1st approx.	$m'(HPbO_2^-)$ 1st approx.
1U	39	0.1059	0.000637	0.001318	0.04360	0.001977
2	19	.1054	.000600	.001240	.04385	.001862
3U	19	.1077	.000651	.001348	.04432	.002020
4S^a	30	.2156	,001667	.003462	.08407	.005192
6S^o	30	.2149	.001595	.003312	.08469	.004968
6U	34	.2184	.001745	.003619	.08429	.005428
7U	35	.2200	.002075	,003556	.08415	.005838
8U	58	.3257	.002784	.005802	.1239	.008702
9U	44	.3244	,003280	.006842	.1215	.01026
10U	44	,3344	.003251	.006823	.1225	.01021
11S^a	33	.3380	.003203	.006681	.1244	.01002
12U	15	.5129	.003694	.007769	.2074	.01165
13	24	.4967	.003403	.007101	.2006	.01065
14U	24	.9676	.006284	.01335	.4026	,02003
15U	16	,9939	,006382	.01349	.4127	.02023
16U	12	1.0013	.007302	.01544	.4037	.02317
17U	12	1.0013	.007736	.01146	.4001	.02469
18S^a	24	1.0392	.007047	.01501	.4293	.02251
19	22	1.6020	.01169	.02536	.4659	.03804

TABLE IV *(Concluded)*

No. of expt.	Days of rotation	0.5023 *M* HCl to 1 *g.* of soln., g.	$PbCrO_4$ to 1 *g.* of soln., g.	$m(CO_3^{--})$ final	$m'(OH^-)$ 1st approx.	$m'(HPbO_2^-)$ 1st approx.
20	12	1.6127	.01055	.02278	.6807	.03416
21	39	1.6266	.01060	.02297	.6854	.03445
22	11	1.7111	.01331	.02868	.6910	.04300
23	22	1 339	.01529	.03341	1.0075	.05012

No. of expt.	$\mu^{1/2}$	$-\log \gamma$ (OH^-)	$-\log \gamma$ (HPO_2^-)	$-{}^1/_4 \log \gamma$ (CO_3^{--})	$m(OH^-)$ final	$m(HPbO_2^-)$ final	Log K_m	Log K
1U	0.222	0 0801	0.1310	0.0830	0.04389	0 001689	−4.574	−5 070
2	.222	.0801	.1310	.0830	.04412	.001588	−4.723	−5.219
3U	.224	.0809	.1320	.0835	.04459	.001731	−4.570	−5.068
4S[a]	.316	.0981	.1880	.1091	.08447	.004792	−4.387	−5.117
5S[a]	.316	.0981	.1880	.1091	.08507	.004590	−4.483	−5.233
6U	.317	.0984	.1885	.1095	.08471	.005015	−4.277	−5.030
7U	,317	.0984	.1885	.1095	.08459	.005392	−4.191	−4.943
8U	.386	.1055	.2318	.1260	.1243	.008255	−4.384	−5.348
9U	,390	.1060	.2340	.1270	.1220	.009714	−3.977	−4.953
10U	.391	.1061	.2345	.1274	.1230	.009682	−4.003	−4.983
11S[a]	.392	.1061	.2350	.1278	.1250	.009505	−4 095	−5.079
12U	.500	.1100	.3000	.149	.2058	.011305	−5.253	−6.575
13	.482	.1100	,2900	.146	.2009	.01032	−5.377	−6.645
14U	.676	....	....	....	.4029	,01977	−6.097	.....
15U	.678	....	....	....	.4131	.01997	−6.151	.....
16U	.687	....	....	....	.4040	.02288	−5.789	.....
17U	.689	....	....	....	.4004	.02438	−5.624	.....
18S[a]	.706	....	....	....	.4340	.02225	−6.068	.....
19	.883	....	....	....	.6661	.03781	−6.222	.....
20	.885	....	....	....	.6809	.03396	−6.524	.....
21	.888	....	....	....	.6900	.03426	−6.545	.....
22	.906	....	....	....	.6913	.04276	−6.069	.....
23	1.076	....	....	....	1.0077	.04994	−6.879	.....

[a] In Expts. 4 and 5 the solutions were rotated for fifteen days at 32°; in Expt. 11, fourteen days at 32°; and in Expt. 18, eleven days at 32°, and then transferred to a thermostat at 25° and rotated for the time indicated in Col. 2.

In Tables I–IV are included all the experiments in which check results were obtained. The agreement is satisfactory, except in Expts. 9, 10 and 11, in which the results are anomalous. The variations of the values of the equilibrium constant appear to be of considerable magnitude owing to the smaller proportion of lead, and therefore of CO_3^{--}. The difficulties of analysis are very great and the principle of the ionic strength is probably not as exact under these conditions as in the other experiments. There is a large multiplication of errors in obtaining log K, but the final value of the free energy change is probably not in error by more than 130 cal. per mole of lead. We shall choose as a final value

$$\log K_{298} = \log (HPbO_2^-)^3(CO_3^{--})^2(H_2O)^3/(OH^-)^7 = -5.10;\ K_{298} = 8 \times 10^{-6}$$

$$Pb_3(CO_3)_2(OH)_2(s) + 7OH^- = 3HPbO_2^- + 2CO_3^{--} + 3H_2O;\ \Delta F^\circ_{298} = 6961 \text{ cal.} \quad (15)$$

Summary

The solubilities of the red and yellow forms of lead monoxide, of hydrated lead monoxide and of basic lead carbonate in dilute aqueous potassium hydroxide solutions at 25° have been determined.

The change of the stoichiometrical equilibrium constant with concentration shows that the activity coefficient of the plumbite ion is about the same as that of the nitrate ion in dilute solutions.

From the extrapolated values of the equilibrium constants, the free energies of solution have been calculated.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PHYSICAL AND CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

THE ATOMIC ARRANGEMENT IN THE CRYSTAL OF ORTHORHOMBIC IODINE

BY PRESTON M. HARRIS, EDWARD MACK, JR., AND F. C. BLAKE

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The crystal structures of few of the non-metallic elements have been fully analyzed by the use of x-rays. Iodine has been studied recently by Ferrari[1] who has determined only the size of the unit cell, nothing being published concerning the arrangement of the atoms in the cell. A complete solution of the iodine structure is of special interest in connection with the question of the existence of molecules in crystals of non-polar substances and of the relationship of atomic to ionic radius.

The results presented by Ferrari were also obtained by the authors and presented in an unpublished thesis[2] at The Ohio State University in August, 1925. The methods used in this work were the same as those of Ferrari.[1] However, the results of the powder photographs obtained cannot be reconciled with those of Ferrari. These will be discussed in detail in the latter part of the present paper.

An extended study of the iodine symmetry was made by means of Laue photographs prepared with various crystal orientations and what is believed to be a unique solution of its structure was obtained in May, 1926. The definition of the structure involves two parameters which must be wholly evaluated from measurements of the intensities of reflection alone. Since the data obtained by the Laue and powder methods were not sufficient for as accurate a parameter determination as was desired, the crystal has since been re-analyzed by the oscillated crystal method.

The parameters have been evaluated from the intensity data in two ways, one being the well-known structure factor method[3] and the other the Four-

[1] Ferrari, *Atti. Accad. Lincei,* *[6]5, 582* (1927).

[2] Thesis for the Master of Arts Degree by P. M. Harris.

[3] Wyckoff, "Structure of Crystals," Chemical Catalog Co , Easton, Pa., 1924.

ier series method as formulated by Duane[4] and used by Havighurst.[5] This investigation thus serves as a test of the efficacy of the Duane method in the determination of parameters in crystals of relatively low symmetry.

Experimental

The cameras employed in the powder method have been described elsewhere.[6] The K_{α_1, α_2} characteristic from a water-cooled molybdenum target (Coolidge tube) was used. In some cases the incident and in other cases the reflected beams were filtered with zirconium oxide in order to remove the K_β line as well as a part of the general radiation. Pure aluminum and pure sodium chloride were used as reference standards, a_0 for the aluminum[7] being taken as 4.0438 Å., as measured in this Laboratory, and a_0 for salt as 5.6280 Å. Correction for penetration was made by the method[7] of Blake.

In the Laue method photographs were prepared with crystal to plate distances both of 4 and of 5 cm. A tungsten target Coolidge x-ray tube as a source of white radiation was operated at peak potentials of from 39 to 55 kilovolts as measured on a sphere gap.

The oscillated crystal photographs were prepared in a cylindrical brass camera of approximately 7.9 cm. radius, using a film 15 cm. wide and held in place inside the camera body at top and bottom by cast iron expansion rings similar to piston rings. The camera was provided with gold slits. The crystal table was mounted on a steel spindle fitted in a 6.3 cm. tapered bearing accurately turned to be co-axial with the body of the camera and actuated by a heart-shaped cam designed to give the crystal a constant angular velocity.[3]

Groth[8] gives the axial ratio for orthorhombic iodine as 0.6644:1:1.3653. The crystal has bipyramidal symmetry (determined by Mitscherlich). V. Federov[9] has given a description of a second crystalline variety of iodine which he found to be monoclinic. V. Kurbatow[10] has investigated the conditions under which the monoclinic modification is formed. He states that the monoclinic form is obtained by sublimation below 46.5°, or by crystallization by rapid evaporation of a volatile solvent such as ether. W. Wahl,[11] who worked with the orthorhombic form, was able to find no transition of the orthorhombic iodine into the monoclinic on cooling to below $-180°$ and considers it improbable that there is such a point.

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[4] Duane, *Proc. Nat. Acad. Sci.*, 11, 489 (1925).

[5] Havighurst, THIS JOURNAL, 48, 2113 (1926).

[6] Havighurst, Mack and Blake, THIS JOURNAL, 46, 2368 (1924).

[7] Blake, *Phys. Rev.*, 26, 60–70 (1925).

[8] Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, Vol. 1, p. 39.

[9] V. Federov, *Z. Krist. Mineral.*, 46, 215 (1909).

[10] V. Kurbatow, *Z. anorg. allgem. Chem.*, 56, 230 (1908).

[11] Wahl, *Proc. Roy. Soc. (London)*, 88A, 352 (1813).

Wahl believes that the ordinary form is stable at all temperatures and that the monoclinic prism is a monotropic form having a marked temperature limit of formation and apparently a low velocity of transformation at ordinary temperatures. He states that v. Federov and v. Kurbatow were unable to determine whether the crystals used were pseudomorphosed, due to the metallic and opaque character of iodine. The crystals used in the present investigation were given several different treatments.

1. Baker's "Analyzed" iodine was used for powder photographs without treatment other than grinding.
2. Iodine from the same source was cooled to about −75° with a mixture of solid carbon dioxide and acetone. The iodine was ground while cold. This method was found to give a finer powder.
3. Iodine was sublimed at temperatures above 75°. Iodine prepared in this way was studied by all three photographic methods.
4. Sublimed crystals were prepared from a mixture of iodine with phosphorus pentoxide, to remove the water vapor. The temperature of the sublimation was above 75°. Iodine prepared in this way was used in both the powder and the Laue methods.
5. Iodine prepared by very rapid evaporation of the solvent (ethyl ether) was used in the powder method. The crystallization in this case took place below room temperature, the evaporation of the ether under reduced pressure cooling the system.

No differences in diffraction patterns prepared from the different samples were observed. Laue and oscillated crystal analysis showed the iodine used to be orthorhombic. Wahl's work is thus confirmed and doubt arises regarding the conditions under which the monoclinic variety of iodine is formed.

Determination of Structure

Gnomonic projections of Laue photographs taken with the x-ray beam perpendicular to the face of the crystal plate indicated that the sublimed crystals used were all tabular on $(010)_G$, where the subscript G refers to the axial ratio as stated by Groth. This is in agreement with the work of Ferrari.[1] Measurements gave an axial ratio $a:c$ agreeing with that of Groth within 1%. A complete analysis of the Laue photographs was then made on this basis and the values of $n\lambda$ calculated were plotted against the observed intensities of the corresponding spots.

The short wave length limit in the white radiation used to produce the Laue photographs, as defined by the quantum equation, $Ve = h\nu$, was never less than 0.2 Å. The analysis of the data on the basis of the one atom cell as calculated from the axial ratio and the density gave values of $n\lambda$ very much less than this. As a result, the computations were repeated for cells having each of the dimensions doubled, one at a time, then two at a time, and then for all three doubled. The last arrangement was the only one of the seven which gave values of $n\lambda$ greater than 0.2 Å. for all planes observed. Evidence of the correctness of these conclusions is given in the accompanying graphs, Fig. 1.

Iodine has a critical absorption limit at 0.374 and silver (in the film) at 0.48 Å. The graphs show clearly that the intensity drops off sharply on the short wave length side of the iodine limit and again on the long wave length side of the silver limit. A similar case (among many others) is that of sodium periodate[12] which shows the iodine and silver critical absorption limits.

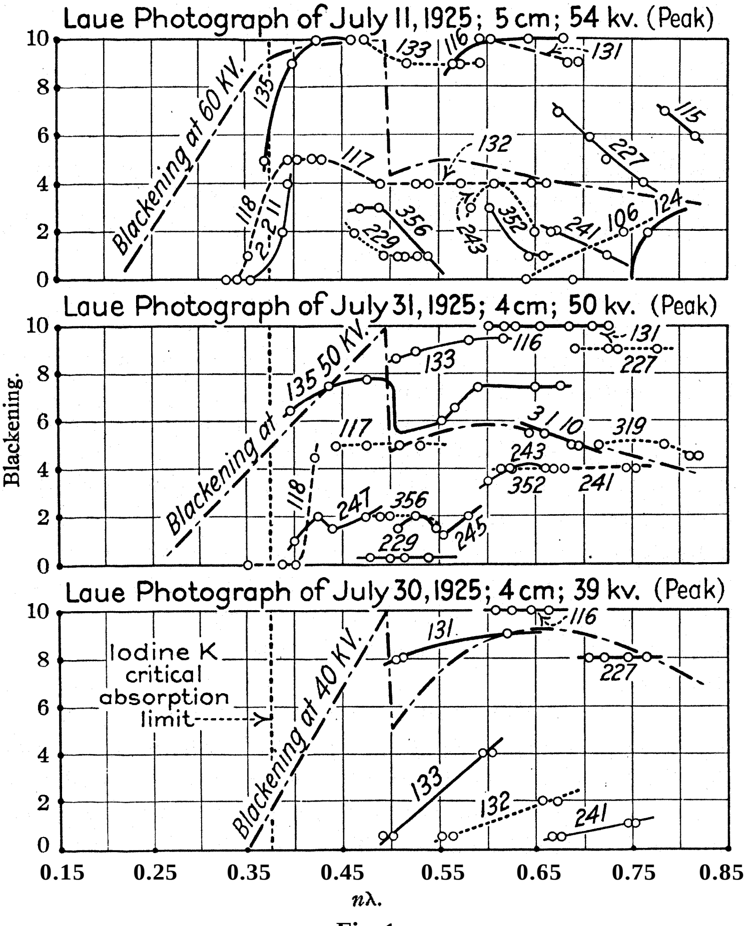

Fig. 1.

Photographs were made by oscillating crystals[13,14] about the c-axis$_G$, and the a-axis$_G$. The values of the primitive translations along the a

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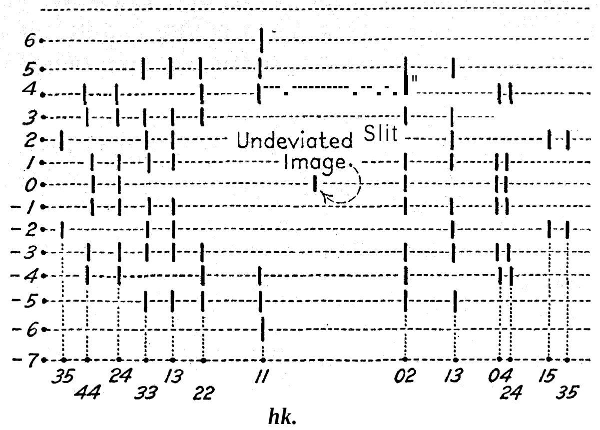
[12] Kirkpatrick and Dickinson, THIS JOURNAL, 48, 2327–34 (1926).

[13] Bernal, *Proc.* Ray. *Soc.*, 113A, 117–160 (1926).

[14] Schiebold, *Fortschritte* Mineral. *Krist.*, *11*, 115–280 (1927).

and *c* axes of Groth calculated from oscillated crystal data agree with the values for the cell chosen from the Laue data. This also confirms the "set-up" of the crystals used with reference to the crystallographic axes. This latter method for the determination of cell size is the most trustworthy known at the present time.[13]



Tracing of photograph of iodine crystal oscillated through an angle of 30° about c axis.

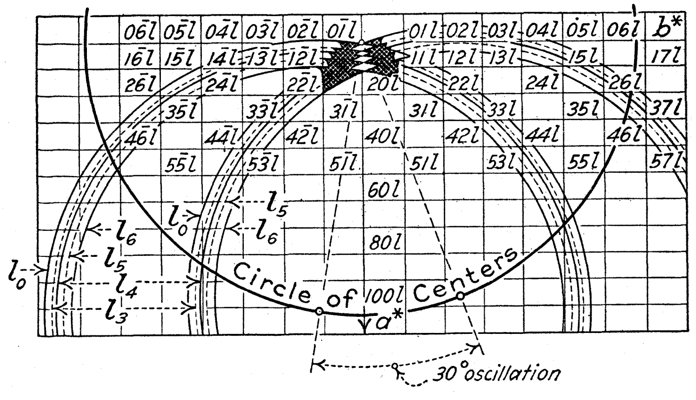


Fig. 2.—Oscillation diagram (about *c* axis). Projections of sections of sphere of reflection at maximum and minimum positions, showing lunes of reciprocal lattice for 1 = 0, = 3, = 4, = 5, and = 6.

An inspection of the accompanying tables and graphs shows that only those planes reflect in the first order which have $(h + k)_G$ even. This indicates[15] that the cell is end-centered on $(001)_G$ (has structure Γ_0).[16]

[15] P. Niggli, "Geometrische Krystallographie des Discontinuums," Borntraeger, Leipsig, 1919, p. 496. See also Bozorth and Pauling, THIS JOURNAL, 47, 1561 (1925).

[16] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Institute Pub. No. 318,* Washington, 1922.

The space groups built on this basis are V_h^{17} . . . . . V_h^{22} inclusive. These are further distinguished by the facts that (1) prism planes having $h + k + l$ even, cannot reflect in the first order for groups V_h^{18}, V_h^{21}, V_h^{22}; (2) prism planes having $h + k + 1$ odd cannot reflect in the first order for V_h^{20} and V_h^{22}. The data (see Table I) show that first order reflections have been obtained from the plane $(403)_G$ and probably $(407)_G$, on Laue photographs. This indicates that the structure is different from V_h^{20} and V_h^{22}; these structures were also eliminated by consideration of the individual cases under them.

TABLE I

OSCILLATED CRYSTAL AND LAUE METHOD INTENSITY DATA

			Oscillated crystal				Laue method First order reflections		
				calculated intensities					
(h	k	l)SQ	obs intensity	u=0 160 v=0.115	0.150 0.119	0 160 0.119	Int.	λ	Photo No
0	0	2	3.0	2.63	0.94	0.94			
0	0	4	30	31.1	32.4	32.4			
0	0	6	2	2.4	0.6	0.6			
0	0	8	9.6	5.1	6.0	6.0			
0	2	0	10.0	5.0	3.0	5.7			
0	2	1	30.6	11.5	12.2	11.1			
0	2	3	40.0	11.6	10.4	9.4			
0	2	4	7.5	1.3	1.3	2.5			
0	2	5	11.8	2.0	3.0	2.7			
0	2	7	20.0	5.1	4.4	3.9			
0	4	0	8.6	4.2	4.2	2.6			
0	4	1	2.4	0.9	1.0	1.7			
0	4	3	2.7	1.3	1.1	2 0	2	0.542	8
0	4	4	3.1	3.0	3.1	2.0			
0	4	7		1.0	0.8	1.4	1	.444	8
1	1	1	16.7	16.8	16.0	13.3			
1	1	2	50	36.8	37.2	40.5			
1	1	3	2 5	3.8	4.8	4.0			
1	1	4	7.5	0.9	0.3	0.4	3	.516	8
1	1	5	2 5	4.1	3.5	2.9	8	.652	8
1	1	6	3 3	6.0	6.6	7.2	10	.499	5
1	1	7		0.4	0.7	0.6	5	.431	1
1	1	8		.9	.3	.4	5	.394	1
1	3	1	17.9	5.6	5.4	4.3	9	.405	5
1	3	2	2.8	1.0	1.0	0.2	4	.384	5
1	3	3	8.9	2.5	3.1	3.4	10	.473	1
1	3	5	13.9	4.7	4.1	4.4	9	.398	11
1	3	6	2.0	0.5	0.5	0.1	3	.431	5
1	3	7	1.6	.6	1.0	1.1	3	.401	5
1	5	2	5.0	8.1	8.2	7.4			
2	0	0	40	81.3	81.3	81.3			
2	0	4	25	20.0	20.5	20.5			
2	2	1	2.5	7.7	8.1	7.4			
2	2	3	16.4	8.7	7.8	7.1			
2	2	4	6.6	1.0	1.1	2.0			
2	2	5	7.4	1.6	2.5	2.3			

TABLE I (*Concluded*)

(*h*	*k*	*l*)$_{SG}$	Oscillated crystal obs. intensity	calculated intensities $u = 0.150$ $v = 0.115$	 0.150 0.119	 0.160 0.119	Laue method First order reflections Int.	 λ	 Photo No.
2	2	7	16.4	4.5	3.8	3.5	6	.450	4
2	4	0	8.1	3.6	3.6	2.2			
2	4	1	2 1	0.8	0.9	1.5	4	.517	5
2	4	3	2 5	1 2	1.0	1.8	5	.470	6
2	4	4	2 9	2 7	2.8	1.7			
2	4	5					2	.487	1
2	4	7					3	.466	1
3	1	1	180	4 5	4 3	3 6			
3	1	2	22	127	129	140			
3	1	3	5.0	1 7	2 1	1.8			
3	1	5	4 0	2t;	2 3	1 9			
3	3	1	8 0	3.9	3 8	4 2			
3	3	2	1 6	0 7	0 7	0.1			
3	3	3	5 0	1 9	2 3	2 6			
3	3	5	8 0	3 7	3 2	3 5			
3	3	6		0 4	0 4	0 1			
3	3	7		.6	.8	.9	3	.655	5
3	5	0		0	0	.0			
3	5	1		0	0	2			
3	5	2	3 9	3 0	3.0	2.7	3	.603	1
3	5	3		0	.0	.1			
3	5	4		2	.1	.1			
3	5	5		0	.0	2			
3	5	6		2 0	2 2	2.0	3	.489	1
3	5	7		0	0	.1			
4	0	0	20	16.2	16 2	16 2			
4	0	4	1 3	9.1	9 5	9 5			
4	0	8	5.0	3 2	3.8	3 8			
4	2	1	1 0	3 7	3 9	3.5			
4	4	0	4.9	2.6	2 6	1 6			
4	4	1	0.5	0 6	0 6	1.1			
4	4	3	2 9	.9	8	1.3			
4	4	4	2.4	2.1	2.2	1.4			
5	1	1	1.0	1.6	1.6	1.3			
5	1	2	1.1	5.1	5.1	5.6			
6	0	0	7.5	6.5	6.5	6.5			
6	0	4	4.5	4.7	4.9	4.9			
6	0	8	0.6	2.2	2.6	2.6			
8	0	0	2.0	3.7	3.7	3.7			
8	0	4	1.2	2.6	2.7	2.7			

Note: Indices $(hkl)_G$ may be obtained from $(hkl)_{SG}$ by interchanging *h* and *k*.

Bearing in mind the fact that the symmetry of the crystal is that of V_h^{17}, V_h^{18}, V_h^{19} or V_h^{21}, a further study of the powder photographs was made, an analysis based on the quadratic form of Runge being used to assign the indices. It was found that the plane $(001)_G$ gave observable reflections in the 4th order only. There is no evidence of a Ist, 2nd or 3rd order although such reflections could have been observed easily had they been present. It should be noted that the glancing angles for all of them are less than 8°, for which reflections the intensities are quite large unless the structure factor is quite small. Also, it was noticed in the Laue photographs that, in general, the intensities of the reflections from the zone $(31l)_G$ pass through a cycle of period 41. Reflections from planes $(310)_G$, $(314)_G$, $(318)_G$ are absent; reflections $(311)_G$, $(313)_G$, $(315)_G$, $(317)_G$ and $(319)_G$ are present and quite strong; reflections from $(312)_G$ and $(316)_G$ have been observed but they are not so strong as those from the planes for which l is odd.

Wyckoff has given the expression

$I \propto (d/n)^{2.35}\ X\ (A^2 + B^2)$, where $A^2 = [\Sigma_s \overline{N}_s \cos 2\pi n\ (hx_s + ky_s + lz_s)]^2, B^2 = [\Sigma_s \overline{N}_s \sin 2\pi n(hx_s + ky_s + lz_s)]^2$ and $\overline{N}_s$ is the atomic number and (x, y, z) are the coordinates of the sth atom in the cell, the summation being taken over every atom in the cell; n is the order of reflection.

The above expression is sometimes designated as the structure factor. An investigation of the structure factor for an S-atom cell, end-centered on $(001)_G$ and having two 4-atom planes perpendicular to the z axis indicates that there is no arrangement with four atoms in the x,y plane which will satisfy the intensity relationships. The only possible way of explaining the absence of the first three orders of reflection from $(001)_G$ is by assuming that there are four 2-atom planes perpendicular to and distributed at nearly equal intervals along the z axis.

The relative intensities of the different orders of $(001)_G$ from oscillated crystal measurements also confirm this. This arrangement is indicated by the data given with regard to the $(31l)_G$ planes. Laue photographs do not show such a cyclic appearance of intensities in the case of the zone (111). Although the (114) plane reflects quite weakly, the (118) gives fairly strong reflections.

All possible combinations of the orthorhombic bipyramidal groups having the observed symmetry characteristics, having also eight atoms per unit cell, and having four planes of atoms distributed along the z axis have been fully investigated, the structure factor being derived where necessary. Since the corresponding planes of the forms $(11l)_G$ and $(31l)_G$ do not show similar intensities, it is evident that the structure factor must be a function of the h_G index. This requires that a parameter lie along the x axis. It may be shown that only the arrangements given by V_h^{18} case (f) and V_h^{17} cases (a) with (c), and (b) with (c) and case (f) satisfy these criteria.

Now V_h^{17} cases (a) with (c), and (b) with (c) are equivalent. A very roughly qualitative investigation of the intensities given by the structure factor for this arrangement shows its complete inadequacy for the explanation of the observed intensities. This is true also for case (f) of V_h^{17}. Therefore the arrangement is that of case (f) of V_h^{18}.

Inspection of the tables for the oscillated crystal data shows that all planes $(hk0)_G$ and $(0kl)_G$ are halved. These halvings demand space group V_h^{18}. This confirms the space group choice. The absences of first order reflections of $(hk0)_G$ are clearly shown on the microphotometer curves. Since the parameter must be taken along the x axis of Groth, the indices of a plane referred to the space group axes have the h and k indices interchanged and will be designated by $(hkl)_{SG}$.

Determination of Parameters

The relative intensities of spots on the oscillated crystal photographs were determined for certain of the vertical "layer lines" (*schichtlinien* of the second kind) by means of a Moll microphotometer. The intensities of other reflections were determined visually, using the photometric measurements as a comparison standard.

The crystals used for the oscillation films were extremely thin, the thickness probably never exceeding 0.01 mm. at the beginning of the exposure and decreasing due to evaporation. (To lower the rate of evaporation, the crystals were sealed in small cells made of microscope cover glasses.) Most of the Laue photographs show streaks indicating that the crystals were quite imperfect. As a result of the imperfections and the thinness of these crystals, both primary and secondary extinction (abnormal absorptions due to crystal perfection) should have been quite small; the effects of these extinctions were therefore neglected. It will be shown later that the accuracy of the parameter determinations by the Fourier series method is nearly independent of the perfection assumed for the crystal.

For single crystals, ideally imperfect, $I \propto F^2 [(1 + \cos^2 2\theta)/\sin 2\theta]$, where[5] I is the intensity of the reflected beam, θ the glancing angle and F the structure factor. In the case of ideally perfect crystals, the intensity of the reflected beam is proportional to the first power of the structure factor.

The oscillation photographs were made by the transmission of the Mo K_α doublet through a crystal plate. The whole crystal was bathed in x-rays. Thus, a factor must be introduced to correct for the position of the crystal at the time of reflection and for absorption in the crystal. Since the crystal plates were so thin that practically no edge effect was introduced, $I \propto jF^2 [(1 + \cos^2 2\theta)/\sin 2\theta] \cos \phi e^{-\mu l}$ where ϕ is the position angle of the crystal at time of reflection, μ the apparent absorption coefficient, l the length of path in the crystal and j the number of times a given plane contributes to a spot. When μ is constant (ideally imperfect crystal), the maximum variations in l for the reflections observed and for a decrease in intensity of one-half due to absorption give a variation of only 15% in the factor, $e^{-\mu l}$. Since for nearly all reflections the factor was practically unity, its effect was neglected. The factor $\cos \phi$ was used, however, ϕ being evaluated graphically. In eight cases the intensities were supplemented by a photograph taken by reflection from a crystal plate. Experimental values of F were computed from the above equation. These data were also supplemented by several values of F from powder method films using the relationship[5] $I \propto jF[(1 + \cos^2 2\theta)/\sin^2 \theta \cos \theta]$. Employing Wyckoff's expression for the intensity of reflection by a crystal plane, we obtain for the arrangement V_h^{18} case (f) (if all the iodine atoms diffract alike)

$$I\ a\ \frac{(d)^{2.35}}{n} \{[1 + \cos \pi kn \cos \pi ln \cos 4\ \pi ukn]\ [1 + \cos \pi kn \cos \pi ln \cos 4\pi vln]\}$$

Curves were drawn for the quantity in brackets for several zones. It was found that the Laue data demanded u and v to be approximately equal to 1/6 and 1/8, respectively. These values were confirmed by data from the oscillation photographs. The values of the relative intensities given by this formula have been calculated for several values of u in the neighborhood of 1/6 and v of 1/8. The results are listed in Table I with observed intensities. The closest agreement seems to be given by u = 0.160 and v = 0.119.

In the determination of the parameters u and v by the Duane Fourier series method we follow the work of Havighurst[5] on the mercurous halides. A simple, end-centered lattice in the orthogonal systems possesses three mutually perpendicular planes of symmetry passing through a common point and therefore may be fully described by a Fourier series consisting of cosine terms only. The electron density of such a lattice, provided it has the same elements of symmetry as the lattice, is given by ρ_{xyz} in

$$\rho_{xyz} = \Sigma_h \Sigma_k \Sigma_l\, A_{hkl} \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz$$

the summations being taken over all integral values of h, k, and l, which have been substituted for Duane's n_1, n_2, and n_3 as have x, y, and z for Duane's X/a, Y/b, Z/c, the x, y, and z thus being used in the space group sense of the fractional part of the cell dimension, the full dimension being taken as unity.

Now the arrangement defined by case (f) of V_h^{18} is, on translation to (1/4,0,0)

$$0, u, v;\ 0, u + {}^1/_2, {}^1/_2 - v;\ {}^1/_2, u, {}^1/_2 - v;\ {}^1/_2, u + {}^1/_2, v$$
$$0, \bar{u}, \bar{v};\ 0, {}^1/_2 - u, v + {}^1/_2;\ {}^1/_2, \bar{u}, v + {}^1/_2;\ {}^1/_2, {}^1/_2 - u, v$$

If we take for the origins of four simple and end-centered lattices the four points having $x = 0$, then the sum of the contributions of the four lattices to the electron density is given by

$$\begin{aligned}\rho_{xyz} = \Sigma_h \Sigma_k \Sigma_l\, [&A^{\mathrm{I}}_{hkl} \cos 2\pi hx \cos 2\pi k(y + u) \cos 2\pi l(z + v)\\ &+ A'_{;:}\ \cos 2shx \cos 2\pi k(y - u) \cos 2\pi l(z - v)\\ &+ A^{\mathrm{III}}_{hkl} \cos 2\pi hx \cos 2\pi k(y + \tfrac{1}{2} + u) \cos 2\pi l(z + \tfrac{1}{2} - v)\\ &+ A^{\mathrm{IV}}_{hkl} \cos 2\pi hx \cos 2\pi k(y + \tfrac{1}{2} - u) \cos 2\pi l(z + \tfrac{1}{2} + v)]\end{aligned}$$

Setting $A' = A^{II} = A'' = A^{IV}$ (assuming the four pairs of I atoms equivalent in diffracting power) and expanding and combining, we have

$$\rho_{xyz} = \Sigma_h\Sigma_k\Sigma_l\, 4A^{I}_{hkl} \cos 2\pi hx \,\{[\cos 2\pi ku \cos 2\pi lv \cos 2\pi ky \cos 2\pi lz]_{(k+l)\ \text{even}} + [\sin 2\pi ku \sin 2\pi lv \sin 2\pi ky \sin 2\pi lz]_{(k+l)\ \text{odd}}\}$$

Since the crystal has a plane of symmetry perpendicular to x and passing through the origin used

$$\rho_{x00} = \Sigma_h\Sigma_k\Sigma_l\, A_{hkl} \cos 2\pi hx$$

Now from the developed expression

$$\rho_{x00} = \Sigma_h\Sigma_k\Sigma_l\, 4A'_{hkl} \cos 2\pi ku \cos 2\pi lv \cos 2\pi kx$$

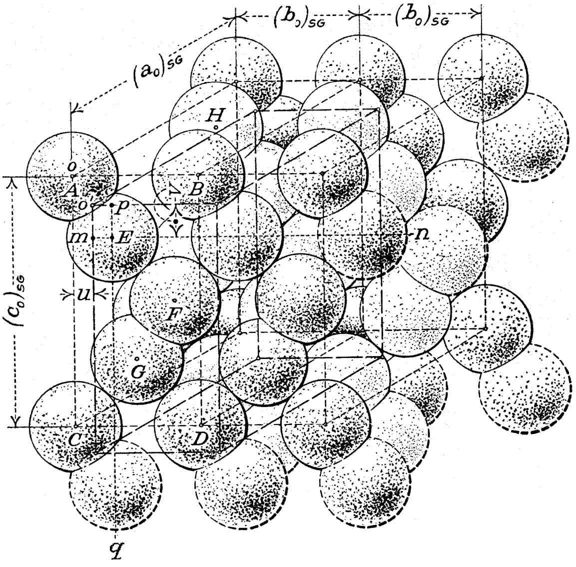
Hence

$$A_{hkl} = 4A'_{hkl} \cos 2\pi ku \cos 2\pi lv \ (\text{for } (k+l)_{\text{even}})$$

and by analogy

$$A_{hkl} = 4A'_{hkl} \sin 2\pi ku \sin 2\pi lv \ (\text{for } (k+l)_{\text{odd}})$$

Using the approximate values of u and v determined by the structure factor method, the signs of the terms have been determined and the series evaluated along $x = 0$, $y = 0.150$, $z = z$, $x = 0$, $y = y$ and $z = 0.115$, corresponding to the lines pq and mn, respectively, in Fig. 3, the results of which are shown in the accompanying graphs, Figs. 4 and 5. It is found that the portions of the curves beyond $z = 0.25$ and $y = 0.30$ are susceptible to considerable change by the omission of only one or two terms, while



Two unit cells shown. Space group V_h^{18}, case (f). Axes of Fourier series by translation of space group to $\frac{1}{4}$,0,0. Atoms in front and back planes heavy; atoms in mid-plane light; atoms in contiguous cells dashed.

Fig. 3.—Structure of orthorhombic iodine.

the position of the main peak is practically unchanged. This suggests that the series converges slowly because of its low symmetry and that the minor peaks are due to the fact that not enough terms have been used to straighten out the flat portion of the curve as well as to certain inaccuracies in the evaluation of the term coefficients.

The series used is slowly convergent also because the F curves for heavy atoms do not approach zero rapidly with increasing glancing angle. In the values of the series coefficients calculated from observed intensity data.

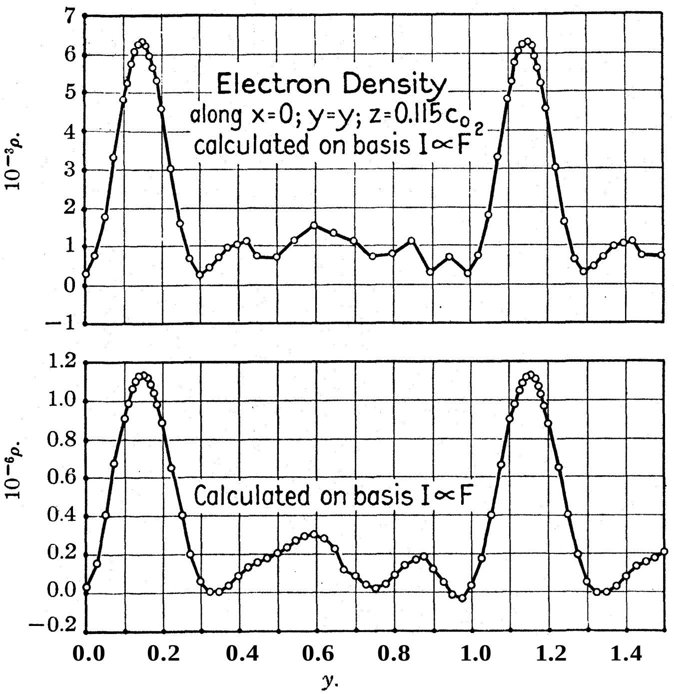


Fig. 4.

the Debye temperature factor has been included, since it could not be evaluated even approximately. This practice, however, increases the rapidity with which the series converges.[17]

The series has also been evaluated for values of the structure factor derived on the basis of the ideally perfect crystal (values of F the squares of the former values). Now each of the coefficients consists of the sum of the squares of the terms which were summed to form the coefficients of the old series. *The resulting curve has its principal maximum at very nearly the same place as before.* The knowledge of this fact is of prime importance, since it makes it evident that in this method of parameter

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[17] Havighurst, *Phys. Rev.*, 29, 9 (1927).

determination the question of crystal perfection is not serious, at least in the case of those parameters corresponding to peaks for the upper portions of which all terms of the series are positive.

VALUES OF PARAMETERS OBTAINED

	Structure factor method	Fourier series method $I \propto F^2$	$I \propto F$
u	0.160	0.150	0.150
v	.119	.117	.115
AE	2.788 Å.	2.703 Å.	2.670 Å.
CG	3.509 Å.	3.538 Å.	3.569 Å.
AH	4.348 Å.	4.348 Å.	4.348 Å.

Referring to Fig. 3 it would appear that the two atoms A and E correspond to a molecule of I_2 and similarly in the case of the two atoms G and F.

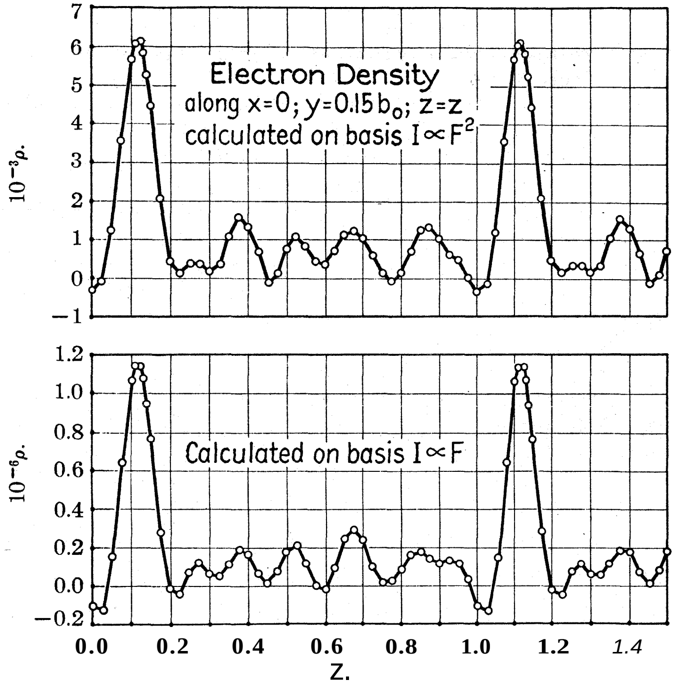

Fig. 5.

The spheres have been drawn so that G osculates C and D. Now the distance AE = GP = $2\sqrt{v^2c_0^2 + u^2b_0^2}$; and the distance CG = DG = $\sqrt{(1/2 - 2v)^2c_0^2 + b_0^2/4}$; and the distance AH = $1/2\sqrt{a_0^2 + b_0^2}$ The values obtained are shown in the above table. Values of iodine atom and ion dimensions calculated from x-ray crystal structure results, on assumption of constant atomic radii, and also calculations from viscosity and other data are shown in the following table.

Iodine Atom and Ion Dimensions

Distance	Source	Value, Å.	Authority
I^- radius	Alkali halides	1.40	W. L. Bragg, *Phil.* Mag, 40, 169 (1920)
	$CsCl_2I$	1.50	Wyckoff, Proc. Nat. Acad. *Sci.*, 9, 33 (1923)
	$CsI(Cs^+ = I^-)$	1 974	Davey, *Chem.* Rev., 2,349 (1926)
	Xe radius, from viscosity of Xe	1.75	Rankine, Pror. Roy. *Soc.* (London). **98A,** 360 (1921)
	Alkali halides	2.10 (approx.)	W. L. Bragg, *Phil.* Mag, [7] 2, 258 (1926)
	Theoretical	2.19	Wasastjerna, *Soc. Sci. Fennica Comm.*, **1,** No. 38, 1–25 (1923)
$(I-I)/2$	Between two SnI_4	2.10^5	Dickinson, This Journal, 45, 958 (1923)
	CdI_2	2.10^5	Bozorth, This Journal, 44, 2232 (1922)
	Viscosity (and if I^- radius = 1.75)	1.40	Rankine (*loc. cit.*)
I atom radius		1.30	Walden, Z. anorg. *allgem. Chem* , 113, 125 (1920)
$Sn-I$	SnI_4	2.63	Dickinson (*loc. cit.*)
$Sn-Sn$	Gray tin	2.80	Bijl and Holkmeyer, Proc. Roy. *Soc.* Ac. Amsterdam, June-Sept. (1918)
I^- radius	SnI_4 and Sn	1.23	
$(I-I)/2$	HgI_2	2 05	Huggins and Magill, This journal, 49,2357 (1927)
$(Hg-Hg)/2$	Hg_2I_2	1.36	Ibid.
$(I-I)/2$	Hg_2I_2	1.71	Ibid.
$(Hg-I)$	Hg_2I_2	2.75	Ibid.
I	$(Hg-I)-(Hg-Hg)/2$	1.39	*Ibid.*
$(I-I)2$ in I	Solid iodine	1.35^2	This paper
Between two I_2		1.769 and 2.17^4	This paper

It appears from the foregoing table that the iodine atom may have several radii of combination. In polar compounds, the radius probably corresponds to an ion radius of approximately 1.77 Å., (CG/2), or 2.17 Å., (AH/2). In the case of non-polar combinations, the radius seems to be approximately 1.35 Å., (AE/2), corresponding, perhaps, to the radius of the next to the outer shell of electrons in the iodine atom. This is in accordance with the anticipation of Rankine.

Finally, in considering the strength of the evidence for the proposed structure, we may say:

(1) No preliminary assumption regarding the existence of molecules has been made, and in the case of the Fourier analysis, the positions of the atoms have been found from a determination of the electron densities. This has placed the solution on as purely analytical a basis as is possible with methods in their present state of development.

(2) Such an ample quantity of data has been obtained that, after analysis, there is much left unused which agrees with the structure assigned. This is well illustrated by the zone (351) on the oscillation diagram of Fig. 2. Only those planes with $l = 0, 1, 2, 3, \ldots\ldots 6$, etc., were in position to reflect whose projections on the diagram were swept over by the circular arc, $l = 1$, in a 30° oscillation of its center along the circle of centers. The diagram thus indicates that all planes of zone 351 for $0 \leqq 1 < 6$ were in position to reflect to the right during the exposure. The structure obtained gives calculated intensities for this zone such that the reflection $(352)_{SG}$ should be the only discernible one with $1 < 6$ (see Table I). A small change in the parameters gives quite appreciable intensity to the other reflections of this zone. The reflection $(352)_{SG}$ is the only one of the group which appears and it is fairly strong.

(3) Although no speculations regarding the size or arrangement of the iodine atoms have been used in the solution, the dimensions of the iodine atom obtained from the structure are in good agreement with the results of other investigators.

The structure proposed is not only a necessary result of the analysis but is also sufficient for the explanation of the large amount of data obtained. The authors feel that such a solution may be said to be unique.

Cell Dimensions from Powder Photograph Data

The powder photographs were analyzed by application of the quadratic form obtained by squaring Bragg's equation and setting

$$\frac{d^2}{n^2} = \frac{1}{h^2/a_0^2 + k^2/b_0^2 + l^2/c_0^2}$$

so that

$$\sin^2 \theta = \frac{\lambda^2}{4}\,(h^2/a_0^2 + k^2/b_0^2 + l^2/c_0^2)$$

Using this equation the indices were assigned by a cut and try method. Table II gives the arithmetical mean of the results of six powder films with values of d/n calculated from cell dimensions obtained from the powder data by an application of the Method of Least Squares. In the case of iodine only those values of d/n were used which seemed to correspond to single lines. All the values used also correspond to fairly low indices.

By this method we obtain $a_{0G} = 4.795$ Å., $b_{0G} = 7.255$ Å., and $c_{0G} = 9.780$ Å., or $a:b:c = 0.6609:1:1.3479$. These cell dimensions give a calculated density of 4.913 g./cm^3. As has been stated, the axial ratio accepted for iodine is $a:b:c = 0.6644:1:1.3653$ (Mitscherlich). Marignac[18] has given the ratio $a:b:c = 1:1.515:2.0586$ which is equivalent to $a:b:c =$

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[18] Marignac, "Handbuch der anorganischen Chemie," Abegg and Auerhach, Leipzig, 1913, Vol. 4, pt. 2, p. 349.

TABLE II

OBSERVED POWDER METHOD DATA COMPARED WITH CALCULATED VALUES

(h	k	l)SG	Observed mean d/n	Number of films	Calcd. d/n	Obs. intensity (visual)	Calcd. $u=0.150$ $v=0.115$	Calcd. 0.150 0.119	Intensity 0.160 0.119
1[a]	1	1	3 698	6	3.702	25	76 8	16.0	13.3
2"	0	0	3.616	6	3.628	25	203	20.3	20.3
1[a]	1	2	3094	6	3096	30	368	37.2	40.5
1"	1	3	2.530	5	2527	5	3.8	4 8	4.0
0[a]	0	4	2 453	6	2 445	10	7 8	8.1	8 1
0[a]	2	0	2 389	2	2.398	v.w.	1.3	0.8	1.4
0"	2	1	2.321	6	2329	8	5 8	6.1	5.6
3	1	1	2104	6	2.108	6	4 5	4.3	3.6
2	0	4	2032	6	2027	10	10.0	103	10.3
3"	1	2	1.978	6	1.975		12.7	129	14.0
2"	2	1	1.964	6	1.960	10	7.7	8.1	7.4
0"	2	3	1.929	6	1.931	7	5 8	5.2	4 7
2	2	2	1 877	2	1.851	v.v.w. broad	0.02	0.01	0 02
4"	0	0	1 809	6	1 814	7	4 1	4.1	4 1
1"	1	5	1.759	6	1.758	6	4.1	3 5	2 9
2"	2	3	1.706	6	1.704	10	8.7	7.8	7 1
1	3	1	1541	6	1.540	7	5.6	5 4	4.3
0"	2	5	1.513	6	1516	8	1.0	1.5	1 4
1	1	6			1.510		6 0	6 6	7.2
1	3	2	1488	2	1.487	v.w.	1.0	1 0	0 2
4"	0	4	1 456	5	1 457	6	4.6	4.8	4.8
4"	2	1	1.432	5	1.431	2	3.7	3.9	3.5
2	2	5	1404	6	1.398	4	1 6	2.5	2.3
1	3	3			1 408		2.5	3 1	3.4
5	1	1	1375	4	1.375	1	1.6	1 6	1.3
5	1	2	3336	5	2.336	5	5.1	5 1	5.6
3"	3	3	1.322	6	1321	w.	3 9	3 8	4 2
3	1	6	1299	3	1.301	w.	4 3	4.7	5.1
6	0	0	1200	2	1.209	w.	1.6	1.6	1.6
0	4	0			1.199		1.1	1.1	0.7

[a] Values used in calculation of cell dimensions; w., weak; v.w., very weak; v.v.w., very, very weak.

0.6601:1:1.359. These different ratios proposed by good crystallographers indicate that the exact value of the ratio is probably somewhat different from either and the value obtained in this work may be much more nearly correct. Mitscherlich's values for the ratio were no doubt obtained from measurements on the good crystals which he describes as having been obtained by the slow air-oxidation of an aqueous solution of iodine in hydriodic acid.[19] It is now known that as much as several per cent. of water may be occluded by iodine crystals formed in the presence of water. The differences in the axial ratios may be due to variations in water content.

As has been stated, in no case were first order reflections obtained from

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[19] Mitscherlich, Pogg. Ann., 98, 554 (1856).

planes having $(h + k)$ odd. Ferrari's Laue data' are in accord with this observation. All of our oscillated crystal data also indicate this, as is shown by the diagram, Fig. 3. The zones $(23l)$, $(34l)$, $(45l)$, etc., were in position to reflect to the left and the zones $(12l)$, $(14l)$, $(23l)$, $(25l)$, $(34l)$, $(36l)$, etc., were in position to reflect to the right during the exposure of the photograph whose tracing is shown. No reflections from these zones are observable.

Ferrari lists values of d/n to which he has assigned the indices (100), (012), (021), (004), (210), (131), (015) and (150), the axial ratio of Groth being used. Of these the only ones which could have other than zero intensity are (021), (004) and (131), since all prisms $(hk0)$ are halved. Ferrari states that the sublimed crystals are tabular on $(010)_G$ (in accordance with our observations). Although Ferrari lists several orders of reflection for this plane in his rotated crystal data (and in our experience it reflects very strongly in the second order), no line corresponding to it is found in his powder data.

The writers employed powder cameras of approximately 330 mm. diameter while Ferrari used cameras about 57 mm. in diameter. The authors also used a comparison standard on every film as well as quite small sample tubes (0.4 mm.), thus obtaining distinct and fairly sharp diffraction patterns.

Since the indices assigned to powder data in this paper are in complete accord with the structure chosen from the Laue and oscillated crystal data, it seems that Ferrari's powder data must be in error.

The authors wish to express their appreciation for a grant from the funds of the American Association for the Advancement of Science.

Summary

1. By use of Laue and oscillated crystal photographs of the ordinary form of solid iodine, the unit cell having orthorhombic bipyramidal symmetry has been found to contain eight atoms. The best values of cell dimensions, obtained by an application of the Method of Least Squares to the observed values for d/n are: $a_0 = 4.795$ Å.; $b_0 = 7.255$ Å.; $c_0 = 9.780$ Å. These correspond to an axial ratio of 0.661:1:1.348 and a density of $4.913/\text{cm.}^3$ (axes chosen according to Groth).

2. The symmetry of the cell is that of space group V_h^{18}, the atoms being located according to the arrangement (f).

3. The values of the two parameters have been determined by use of both the structure factor method and the Fourier series method of Duane. By the latter, values of $u = 0.150$ and $v = 0.117$ are obtained. The parameter u is to be taken along the x-axis of Groth and the parameter v along the z-axis.

4. In the determination of the parameters by the Fourier series method,

the abnormal absorption effects due to crystal perfection are shown to be negligible in the case of iodine.

5. The atoms are found to be grouped in molecules of I_2. The distance between centers of the two atoms in one molecule is found to be 2.70 **Å**. Distances of closest approach of centers of 3.54 and **4.35 Å**. exist in the crystal. Either of these may correspond to the ion radius of iodine.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY AND FROM THE WEST VIRGINIA GEOLOGICAL SURVEY]

A NEW EQUILIBRATOR: A DEVICE FOR THE DETERMINATION OF THE DISTRIBUTION RATIO OF A VOLATILE SOLUTE BETWEEN TWO MISCIBLE SOLVENTS

BY GRINNELL JONES AND B. B. KAPLAN

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In the course of an investigation on the normal potential of the iodine electrode to be described in a subsequent paper it became necessary to determine the free iodine present in a solution containing potassium iodide, iodine and tri-iodide. For this purpose we invented a device which we call an equilibrator, which permits the determination of the distribution ratio of a volatile solute between two miscible solvents. Since it is planned to use this device in several other researches in this Laboratory it seems desirable to describe it in a separate paper.

The equilibrator is a closed glass apparatus without mechanical valves and contains no liquids to produce seals except the two separated solutions under investigation and yet by mere rotation it causes a continuous circulation of gas or vapor so that it bubbles through the two solutions in turn for as long as the rotation continues. This ensures equality of vapor pressure of the common volatile constituent from the two separated liquid phases if the rotation is continued long enough. After equilibrium has been established the two solutions are separately available for analysis and for any other use that may be desired.

The design and mounting of the equilibrator will be clear from the figure, which shows the plan or top view, end elevation, side elevation and mounting in the thermostat. The essential features are two tubes (A) and (B) which make an angle of about 14 circular degrees with each other in a vertical direction and which are connected at each end by glass tubes (C) and (D) each provided with a ground glass stopper (I) and (J). The stoppers may be replaced at the end of the run by delivery tubes of the type (L) shown in the figure which are ground to fit the same openings. The connecting tubes permit free circulation of the vapor but prevent mixing of the solutions. They are bent inward and upward as shown so that centrifugal force and gravity will help to prevent spattering. It was repeatedly demonstrated by methods which are so obvious as not to require detailed explanation that these connecting tubes are effective in preventing mixing of the two separated solutions by spattering. However, if the equilibrator is started or stopped too suddenly the momentum of the liquids may carry the liquids over the peak of the connecting tubes. In our apparatus tubes (A) and (B) each have a capacity of about 300 cc.

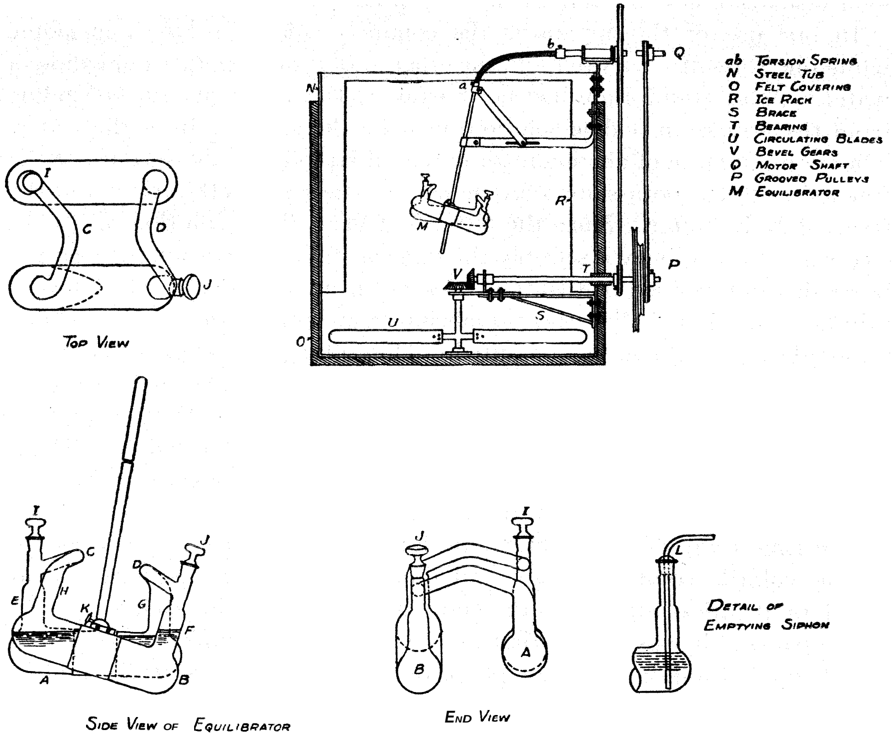

Fig. 1.

The equilibrator is mounted in a brass bracket (K) (not shown in the top view or in the end view) on a shaft so that the shaft bisects the angle between the two glass tubes (A) and (B). This shaft is then mounted so that it can revolve in a bearing at an angle with the vertical which is adjustable. The angle with the vertical should be greater than one-half the angle between the two glass tubes. Our apparatus which had an angle of 14 degrees between the two glass tubes is most effective as an automatic circulating pump when the shaft is mounted so that the angle between the shaft and the vertical is 11 degrees. The shaft is then connected to a horizontal driving shaft by means of a flexible coiled phosphor bronze torsion spring or by a universal joint. A suitable speed is sixteen rotations of the equilibrator per minute. Instead of rotating the equilibrator it may be rocked back and forth on a horizontal axis at right angles to the tubes (A) and (B) and will then function equally well as a circulating pump.

For use at 0° a cylindrical rack (R) made of coarse mesh wire screen is placed inside of and concentric with the tub. By filling this rack with ice and stirring vigorously the entire tub can be kept at 0°. A cover with heat insulation not shown in the figure is used.

In our use of the apparatus the common volatile solute was iodine while one solvent was water and the other a solution of potassium iodide in water. After equilibrium had been attained the vapor pressure of iodine from the potassium iodide solution must be the same as from the water. Therefore, in spite of abundant formation of tri-iodides, the activity of the free iodine in the potassium solution must be the same as the activity of the free iodine in water, Since the latter is a very dilute solution of a non-electrolyte, its activity is sensibly the same as its concentration, which may be readily determined by titration. From the analysis of the solution containing potassium iodide the equilibrium constant of the iodine–iodide–tri-iodide reaction can be computed. This solution of known iodine activity and composition was used in galvanic cells with a platinum electrode for the measurement of the normal potential of the iodine electrode and for measurements of the free energy of formation of silver iodide. These data, which give a proof of the usefulness and reliability of the equilibrator, will be published in the near future.

The time required to attain equilibrium depends on the vapor pressure of the volatile solute, the size and dimensions of the equilibrator and speed of rotation and must therefore be determined in each case. In our apparatus it was proved that pure water can be completely saturated with iodine through the vapor phase in twenty-two hours at 25° and in fifty hours at 0° with 16 rotations per minute. This is a maximum time for iodine, as less time will be required with unsaturated solutions. Moreover, it is possible to add in advance the approximate amount of iodine required to give within 10% of the concentration expected at equilibrium and thus shorten the time necessary to attain equilibrium.

The new equilibrator makes it possible to determine the distribution ratio of any volatile solute between two miscible solvents, whereas the usual method of determining distribution ratios is applicable only to solvents which are immiscible or incompletely miscible. Partial mutual solubility, however, complicates the interpretation of the data. If the solvents are sufficiently non-volatile the new equilibrator avoids this difficulty. Emulsification of the two solvents may make a sharp separation difficult or impossible and thus cause errors in the old method but this difficulty is avoided with the equilibrator.

An even more important field of usefulness, or at least one of greater interest to us, is for the determination of the distribution ratio of a volatile solute between a pure solvent (not necessarily non-volatile) and a solution of a non-volatile solute in the same solvent. The distribution of iodine between pure water and a solution of potassium iodide is of this type. Of course in this case there will be some distillation of water into the potassium iodide solution, thereby diluting it slightly, but this distillation is very slow and if in any particular case the distillation is rapid enough to be significant this merely makes it necessary to analyze the solution for the non-volatile solute at the end of the run instead of depending on the known composition of the original solution.

A similar study of the distribution of bromine between water and aqueous solutions of potassium bromide is now in progress in this Laboratory. The apparatus seems suitable for the study of the distribution of carbon dioxide between water and any salt of carbonic acid from which conclusions as to the concentration or more strictly of the activity of the free acid in the solutions of its salt may be drawn and hence the dissociation constants of the acid can be computed. Similarly the distribution of sulfur dioxide between water and solutions of its salt can be studied. The hydrolysis of sulfides can be determined with distribution experiments with hydrogen sulfide. The amount of free ammonia formed by hydrolysis of any of its salts can be found and hence the dissociation constant of the acid determined or the equilibrium between ammonia and its complex compounds of the type $Ag(NH_3)_2^+$ can be determined.

Summary

A description is given of a new device, called an equilibrator, which by mere rotation acts as an automatic circulating pump, forcing a gas or vapor to bubble continuously and in turn through two separated liquids.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE USE OF PINACHROM AS A ONE COLOR INDICATOR

BY I. M. KOLTHOFF

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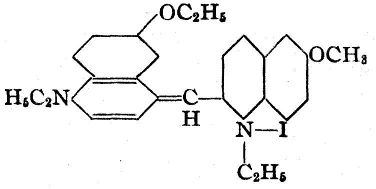
1. The one color indicators described by L. Michaelis and his collaborators are colorless at the acid side and yellow at the alkaline side of their color change interval. In many cases it would be more advantageous to have one color indicators with a more pronounced color change as, for example, phenolphthalein. In this relation, the properties of some methoxytriphenylcarbinols have been described.[1] Also the application of quinaldin red with an indicator constant of $2.70 - 0.007\ (t - 20^\circ)$ may be mentioned.[2]

Besides m-nitrophenol we have no useful one color indicator for the P_H determination in the neighborhood of the neutral point. As m-nitrophenol has some disadvantages, we made a special study of the behavior of cyanin and its derivative, pinachrom. The cyanin, which changes from colorless at the acid to blue at the alkaline side, has the disadvantage of being very unstable in solution, which is a serious objection against its general use.

The pinachrom, however, proved to be an excellent indicator and can be highly recommended for P_H determinations near the neutral point. The pinachrom is used as a sensitizer in photography according to the tables of G. Schultz,[3] No. 611, where more literature about the preparation and properties of this compound can be found.

Pinachrom (M) is p-ethoxyquinaldin-pethoxyquinolin-ethylcyanin. It is very slightly soluble in water but is soluble in hydrochloric acid, forming a colorless liquid.

Probably the formula is



The substance is a weak base with a molecular weight of 518.

2. In my investigations, I used a pinachrom obtained from Farbwerke Meister Lucius and Bruning Hoechst a/M. A 0.1% solution in 70% alcohol was prepared. It has a dark violet color. Another solution was made in which one of the basic groups was neutralized by hydrochloric

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[1] Kolthoff, THIS JOURNAL, 49, 1218 (1927); Lund, *ibid.*, 49, 1346 (1927).

[2] See McClendon, *J. Biol. Chem.*, 59, 437 (1927); Kolthoff, *Biochem. Z.*, will appear in 1928.

[3] G. Schultz, "Farbstoff-Tabellen," 6 Aufl., 1923; Rowe, "Color Index," 1927, 1st ed., No. 807.

acid: 100 mg. of indicator is dissolved in 40 cc. of alcohol, 1.9 cc. of 0.1 N hydrochloric acid is added and the solution is made up to a volume of 100 cc. with water. This solution has a weak violet color. It was kept in a Pyrex bottle. In liquids with a very small or no buffer action—as in distilled water—the neutralized solution should be used; otherwise it is immaterial which solution is employed. The indicator has a color change interval between P_H 5.6 (faintly pink) and 8.0 (deep red-violet). When using 0.1 cc. of indicator in 10 cc. of buffer mixture, the solution is colorless at a P_H of 5.4 and has a very weak red-violet color at a P_H of 5.6. The reaction between the base and the hydrogen ions does not take place instantaneously. After the addition of the indicator, it is necessary to wait at least two minutes before the comparison is made.

When using the indicator without applying buffer mixtures its dissociation constant or hydrolysis constant should be known. Prom the equation $BOH + H^+ \rightleftarrows B^+ + H_2O$, the following expression is derived: $[(BOH)\ (H^+)]/(B^+) = K_h$, where K_h is the hydrolysis constant (or indicator constant), (BOH) is the concentration of the red-violet colored undissociated base and (B^+) the concentration of the colorless form.

Then $(H^+) = [(B^+)/(BOH)]\cdot K_h$.

In determining K_h, 0.4 cc. of 0.02% indicator solution in 40% alcohol was added to 10 cc. of freshly prepared phosphate buffer solution (according to W. M. Clark) and the color was compared with standards of known amounts of 0.002% indicator in 0.01 *N* sodium carbonate solutions. The 0.002% indicator solution was prepared in 0.001 N hydrochloric acid and is colorless.

The alkaline solutions of the indicator cannot be kept, as they are unstable. The free colored base itself is very slightly soluble in water and precipitates after standing for a short time. An interesting phenomenon was observed in preparing the alkaline solution used for comparison. If the tube is violently shaken after adding the indicator, a red froth is formed. This test gives a very simple demonstration of the adsorption of a substance in the interface water-air. After the froth has settled, the upper layer of the solution has a dark violet color, whereas the bulk of the liquid is almost colorless. If the violet layer is mixed with the rest of the solution, the resulting liquid has a much less deep color than it had originally after careful mixing of the indicator solution with the dilute sodium carbonate solution. This striking difference is caused by a precipitation of the indicator base by shaking. Almost all of the indicator is collected in the froth and, as the free base is slightly soluble, it forms a film on the water surface after the froth has settled and does not dissolve any more in the water.

Different tests have been made to prove that the decolorization was not due to an oxidation of the indicator. If the liquid after shaking is acidified and made alkaline, then the original color is restored. Moreover, it can be shown that during the shaking of the alkaline indicator solution, a small part of the base is adsorbed by the glass walls of the Pyrex glass tube. If the alkaline indicator solution is shaken until the solution is almost colorless and then alcohol added, the insoluble film of the free base can be observed. After mixing, the original color strength is restored (the comparison is made in a solution with the same amount of alcohol), If the experiments are repeated in an alkaline solution in 40% alcohol, a colorless froth is formed on shaking, and the color of the solution does not change. This test gives a simple demonstration of the replacing action of a capillary active substance on the adsorption of another capillary active substance.

It should be remarked here that a strongly alkaline solution of the indicator (in sodium carbonate or 0.05 N sodium hydroxide) is partly oxidized after a few days' standing.

The experiments described show that the alkaline solutions for comparison should be made by carefully mixing the indicator with the dilute sodium carbonate solution. If shaking is avoided, no troubles are encountered and reproducible results are obtained. The liquids for comparison, however, must not be kept longer than one hour. Addition of alcohol is not to be recommended, as it changes the shade of color.

In the buffer solutions with a P_H between 5.6 and 8.0, the violet color is stable much longer so that it is often of advantage to perform the colorimetric determination of P_H in the ordinary way with buffer mixtures.

In the following table are given the results of the determinations of K_h at different P_H. It is evident that in respect to its properties as an indicator pinachrom behaves as a mono acid base, the monovalent cations being colorless.

TABLE I

HYDROLYSIS CONSTANT OF PINACHROM AT 22°

P_H	$\frac{[BOH]}{[B^+]}$	$\frac{[BOH]}{[B^+]}[H^+] = K_h$	P_H	$\frac{[BOH]}{[B^+]}$	$\frac{[BOH]}{[B^+]}[H^+] = K_h$
6 0	0.185/3.805	4.8×10^{-8}	7.0	1.32/2.68	4.9×10^{-8}
6.2	0.29/3.71	5.0×10^{-8}	7.2	1.85/2.15	5.0×10^{-8}
6.4	0.43/3.57	4.8×10^{-8}	7 4	2.25/1.75	4.9×10^{-8}
6.6	0.62/3.38	4.7×10^{-8}	7.6	2.65/1.35	4.9×10^{-8}
6.8	0.96/3 04	5.1×10^{-8}		Average K_h =	4.9×10^{-8}

The average value for Kt, at 22° is equal to 4.9×10^{-8}, or $PK_h = 7.31$, corresponding to a dissociation constant of 2 04 $\times 10^{-7}$, or $PK_b = 6.69$.

The temperature modulus of K_h is rather large, the color of the indicator increasing at higher temperatures. From measurements in phosphate buffers between 20 and 40° it was found that $PK_h = 7.34 + 0.013 (20° - t)$.

Pinachrom has the advantage of having a negligibly small salt error at very low salt concentrations. This may be derived from the results of Table II. A Clark buffer solution was diluted with carbon dioxide free water and the P_H of the successive dilution was measured with the hydrogen electrode and in a colorimetric way with pinachrom as indicator. The comparison of the color was made with other freshly prepared Clark's buffers.

There was no difference between the behavior of the unneutralized and the neutralized indicator solution.

TABLE II

SALT ERROR OF PINACHROM AT SMALL SALT CONCENTRATIONS

Buffer soln.	PH with hydrogen electrode	PH with pinachrom
Original Clark buffer soln., salt content		
0.08 N	6.99	..
.04 N	7.06	7.05
.016 N	7.14	7.13
.008 N	7.17	7.18
.004 N	7.18	7.20
.0016 N	7.19	7.22

Practically there is no salt error at very small electrolyte content. The PH of the Minneapolis tap water was determined with the neutralized and unneutralized pinachrom solution. Both indicated the same PH of 7.48, whereas with neutralized solution a value between 7.45 and 7.50 was found. Hence the pinachrom is very useful for the determination of the *PH* of tap water and has distinct advantages over m-nitrophenol, which has a rather high "acid error."

The pinachrom can also be used for testing the quality of distilled water. As the latter has no buffer action at all, it makes some difference whether the unneutralized or neutralized indicator solution is used. The ordinary distilled water in this Laboratory gave with the unneutralized indicator solution a PH of 6.4, and with the neutralized solution a value of 5.95. With the sodium salt of methyl red a *PH* of 5.95 was found. Hence in this case the neutralized indicator should be used, as the solution of the base itself develops basic properties in the unbuffered water.

Probably the indicator will also be useful for the determination of the *PH* in blood serum and milk. So far, however, no measurements on the protein error have been made. In the presence of large amounts of salts pinachrom indicates a too acid reaction, in agreement with its basic character.

A Clark buffer solution with a *PH* of 6.8 was ten times diluted and different amounts of potassium chloride were added. The *PH* of the mixtures was measured with the hydrogen electrode and in a colorimetric way.

TABLE III

SALT ERROR AT LARGER SALT CONCENTRATION

Solutions	PH with hydrogen electrode	PH with pinachrom	Correction in PH for salt error
0.007 N buffer + 0.1 N KCl	6.71	6.58	+0.13
.007 N buffer + .25 N KCl	6.59	6.37	+ .22
.007 N buffer + .5 N KCl	6.48	6.18	+ .30

I also tried to make a mixed indicator[4] with some dyestuff in order to get a sharp color change at a special PH. The best results were obtained with

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[4] See Kolthoff, *Biochem. Z.*, 189, 26 (1927), where other literature is discussed.

a mixture of 2 parts of 0.1% pinachrom and 1 part of 0.1% malachite green (or methylene green). At $P_H = 6.0$ the color is green; at $P_H = 7.0$ and 7.2, blue; at P_H 7.4, violet; at 7.6 red-violet. The application of this mixed indicator does not give many advantages.

Summary

1. Pinachrom is an excellent one color indicator for the determination of P_H between 5.8 and 7.8. $PK_h = 7.34 + 0.013(20° - t)$.

It is recommended for the determinations of P_H in tap water and distilled water.

2. The salt error at low electrolyte content is negligibly small; at higher salt concentrations pinachrom indicates a too acid reaction.

3. A simple test is described by which the adsorption of a substance at the interface water–air, and the increased concentration of the capillary active substance in this interface can be shown.

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THE REDUCTION OF COLUMBIC ACID. I

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Introduction and History

The investigation of columbium and tantalum-bearing minerals began in 1801 when Hatchett,[1] in a black mineral from Massachusetts, afterwards named Columbite, found a new metallic oxide, "Columbium oxide." About the same time Ekeberg,[2] in a similar mineral from Kimit in Finland, called Tantalite, and in another from Ytterby in Sweden, named Yttrotantalite, detected a new oxide called "Tantalum oxide."

Due to the very close similarity in the chemical behavior of columbic and tantalic acids, and their frequent occurrence together in minerals, there existed up to the year 1865 considerable doubt as to the existence of more than one acid. Some believed them to be identical, while others attributed the observed differences in respective properties to the presence of two other elements, "Pelopium" and "Dianium."

It was not until 1865 that the compositions of columbite and tantalite were established. Marignac,[3] then, in his classic researches on columbium and its compounds, proved conclusively that all columbites and tantalites contained columbic and tantalic acids. Since that time, by far the greater part of the work done on columbium concerned either the prepara-

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[1] Hatchett, *Phil. Trans. Roy. Soc*, 92, 49 (1802).

[2] Ekeberg, *Ann. chim.*, 43, 276 (1803).

[3] (a) Marignac, *Ann. chim. phys.*, [4] 8, 1 (1865); (b) [4] 8, 49 (1865).

tion of compounds or the analytical separation of it from tantalum and other associated elements.

Columbic acid unlike tantalic acid gives upon reduction with zinc and mineral acids blue solutions. This color change attracted the attention of a number of investigators, among the earlier of whom were Wöhler,[4] Nordenskjöld,[5] Rose,[6] Blomstrand[7] and Marignac.[8] Although these researches produced nothing definite so far as the chemistry of columbium was concerned, except the obtaining of these colored solutions, yet they furnished a basis upon which the volumetric methods of Osborne,[9] Levy,[10] Giles[11] and Metzger and Taylor[12] were developed and proposed to replace the tedious gravimetric procedure of Marignac,[3] which at best was limited to an accuracy of plus or minus one part in one hundred. Both speed and accuracy were claimed for the above methods. Recently, however, Schoeller and Waterhouse[13] questioned the reliability of these volumetric methods because the results depended upon empirical factors rather than stoichiometric relations. They claim that the values of these factors will vary with the slightest alteration of the experimental conditions upon which the extent of reduction depends and the determinations are fundamentally based.

Osborne[9] in his work states that with acids of low concentration zinc yields a blue solution and that with acids of high concentration a brown solution is obtained. Metzger and Taylor observed that with zinc in hot dilute sulfuric acid solutions of columbium, a blue color is first obtained which rapidly changes to brown. Although attempts were made by some of the above earlier investigators to isolate the reduction products, their efforts were unsuccessful.

In 1896 Pennington,[14] in an endeavor to devise a separation of columbium from titanium, subjected an aqueous solution of $2KF\cdot CbOF_3\cdot H_2O$ to electrolysis and obtained a blue precipitate which was probably a lower hydrated oxide of columbium. No attempt, however, was made to determine its composition.

The electrolytic reduction of columbium pentachloride in concentrated sulfuric and hydrochloric acids was investigated by Ott[15] while he was

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[4] Wöhler, *Ann. Pogg.*, **48**, 93 (1839).

[5] Nordenskjöld, Gmelin-Kraut, Carl Winter, Heidelberg, 1928, Vol. VI (1), p. 219.

[6] Rose, *Ann. china. phys.*, *Pogg.*, 112,475 (1860).

[7] Blomstrand, Gmelin-Kraut, Carl Winter, Heidelberg, 1928, Vol. VI (1), p. 220.

[8] Marignac, *Ann. chim. phys.*, [4] **13**, 30 (1867).

[9] Osborne, *Am. J. Sci.*, [3] 30, 331 (1885).

[10] Levy, *Analyst*, **40**, 204 (1905).

[11] (a) Giles, *Chem. News*, *95*, *1* (1907); (b) 99, 1 (1909).

[12] Metzger and Taylor, *J. Soc. Chem. Ind.*, *28*, 818 (1909).

[13] Schoeller and Waterhouse, *Analyst*, 49, 215 (1924).

[14] Pennington, THIS JOURNAL, **18**, 67 (1896).

[15] Ott, *Z. Electrochem.*, 18, 349 (1912).

attempting to prepare compounds containing trivalent columbium. He found that when columbium pentachloride was reduced in concentrated hydrochloric or sulfuric acid or in an alcoholic solution of anhydrous hydrogen chloride, reddish-brown to black solutions were obtained which he stated contained trivalent columbium. Sodium columbate in an hydrochloric acid solution yielded on reduction a green solution which, as he observed, contained quadrivalent columbium. Fused K_2CbOF_3 yielded on electrolytic reduction a bluish-black product which also seemed to contain quadrivalent columbium. When columbium pentachloride was reduced in concentrated sulfuric acid at a platinum cathode, a blue solution was obtained which appeared to contain a compound of tetravalent and pentavalent columbium corresponding to the oxide Cb_3O_7 or $Cb_2O_5 \cdot CbO_2$. No definite solid compounds, moreover, could be isolated from the hydrochloric acid solutions; but from the concentrated sulfuric acid solution, in the presence of ammonium sulfate, reddish-brown crystals were obtained which had the probable composition indicated by the formula $Cb_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. These crystals, however, could not be quite freed from adhering sulfuric acid. The sulfuric acid solutions of columbium pentachloride employed by Ott throughout his investigation contained approximately 1% of columbium and about 85% of sulfuric acid. No variation of concentration was made nor were experiments performed with solutions of pure columbic acid in sulfuric acid.

Furthermore, in an extended review of the literature, no work was found which furnished definite fundamental information concerning the reduction of columbic acid under conditions whereby the influencing factors were studied and the chemical relations established.

Accordingly, therefore, a research on the reduction of columbic acid was planned and the results given below furnish information on the following points: (a) the solubility of columbic acid in sulfuric acid; (b) the most favorable conditions for preparing a stable and relatively concentrated solution of columbic acid in sulfuric acid; (c) the conditions under which the pentavalent columbium in solution (b) can best be reduced to trivalent columbium.

Experimental

Chemicals.—All chemicals employed throughout this investigation were of the purest grade obtainable. They were further treated by recrystallization from water or by other suitable means of purification, when essential to the purity of the final product.

Columbic Acid.—It was practically impossible to obtain a grade of columbic acid of sufficient purity to warrant its use in this research; so the mineral columbite, which is the most plentiful source of columbium, was used as the starting material for the preparation of pure columbic acid. Because of its importance in this investigation, the method of preparation will be outlined below.

The mineral was first subjected to a qualitative and a partially quantitative analysis to determine approximately the composition. Fifty-three per cent. of Cb_2O_5, 21% of

Ta_2O_5, together with FeO and MnO and small quantities of TiO_2, SiO_2 and SnO_2 were found.

The preparation of pure columbic acid may be divided into two parts.

(a) The Preparation of K_2CbF_7.—The procedure followed was that described by Hall and Smith[16] with certain modifications designed to improve the manipulations. This procedure, which is a further modification of the original method proposed by Marignac, is based upon the different solubilities of potassium fluotantalate and the corresponding columbium compound. Five kilograms of the mineral columbite, ground to 150-mesh, were fused in 100-g. lots with potassium pyrosulfate. Each fusion was made in a large platinum dish, as follows: 400 g. of potassium pyrosulfate was melted in the platinum dish and 100 g. of the finely powdered mineral was added slowly in small portions. Each portion was allowed to fuse completely before the next was added. The melted mass was stirred with a platinum rod. This part of the procedure consumed approximately two hours before all of the mineral was added and a clear and quiet fusion was obtained. After the dish was cooled and the melt was removed, the operation was repeated.

When the fusions were completed the combined melts, broken into small pieces, were digested in distilled water for several days to effect complete disintegration. Mechanical stirrers were used to keep the mixture well agitated. From time to time the precipitated impure columbic and tantalic acids were allowed to settle so that the supernatant liquid could be replaced by distilled water. By t s procedure most of the titanium, the most difficult element to separate from columbium, arid tantalum were removed together with other impurities which went into solution.

After several days of the preceding treatment, the supernatant liquid was replaced by a molar solution of ammonium sulfide and mechanically stirred for several days. Then the ammonium sulfide solution was removed and the precipitated columbic and tantalic acids were washed alternately with dilute ammonium hydroxide and molar sulfuric acid till the washings were free from iron by the ferrocyanide test.

Thereupon the precipitated acids were washed on a Buchner funnel with distilled water, transferred to a platinum dish and taken into solution with a 40% hydrofluoric acid solution After sufficient digestion the acid solution was filtered through ordinary filter paper supported on a hard rubber funnel surrounded by a hot water coil, thereby removing the undecomposed mineral and potassium fluosilicate. To the filtrate in a large hard rubber dish a solution of potassium hydroxide was added to precipitate the less soluble potassium fluotantalate, which was removed by filtration. The potassium fluocolumbate left in the solution was further purified to free it from titanium, tin, tungsten, tantalum, silicon and iron, likely to be present at this point in the process, by a method described below.

(b) Purification of K_2CbF_7 and its Conversion to Columbic Acid.—The procedure followed to effect the purification of K_2CbF_7 and the formation of columbic acid was that outlined by Hall and Smith[16] and Balke and Smith [17]

Four crystallizations from aqueous hydrofluoric acid containing about 20% of the anhydrous acid were sufficient to remove such impurities as tin, tungsten, iron and titanium. The last traces of tantalum were removed by baking the double fluoride as directed by Hall and Smith.[16] The purified double fluoride was dissolved in water in a platinum dish and the solution boiled for several days. K_2CbF_7 was thus changed to $K_2CbOF_5 \cdot H_2O$, which was finally baked for several hours, dissolved in water and filtered through filter paper on a hard rubber funnel surrounded by a hot water jacket. This

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[16] Hall and Smith, THIS JOURNAL, 27, 1369 (1905).

[17] Balke and Smith, *ibid.*, 30, 1637 (1908).

operation was repeated until the insoluble residue, when dissolved in hydrofluoric acid, indicated the solubility of potassium fluoxycolumbate. This occurred usually after three treatments.

A possible trace of silica was removed in the conversion of the potassium fluoxy columbate to columbic acid by heating the $K_2CbOF_5 \cdot H_2O$ with a large excess of concentrated sulfuric acid until very little acid was left. This was necessary to remove all traces of hydrofluoric acid. The solution was then cooled and carefully diluted with distilled water. The resulting mixture was made faintly alkaline with ammonium hydroxide, the excess of which was removed by boiling. The precipitated columbic acid was filtered, washed with distilled water until the washings no longer gave a test for sulfates and then dried in a Freas oven at 50°. The final product was found to contain approximately 17.5% of water. When columbic acid was dried at 100°, we found, as stated generally in the literature, that it retained varying amounts of water, depending upon its physical character.

The method of Balke and Smith[17] for preparing pure columbic acid has been shown to be thoroughly reliable by Barr,[18] who subjected material purified by this method to a spectroscopic analysis. Further confirmation was obtained by Hildebrand[19] through the examination of the arc spectrum of the material.

Solubility of Columbic Acid in Sulfuric Acid

Although it is frequently mentioned in the literature that columbic acid is soluble in concentrated sulfuric acid, nevertheless no results were found to show the extent to which it is soluble. Whereupon, after making a number of preliminary experiments, the following procedure was developed to determine the solubility of columbic acid in sulfuric acid.

Procedure.—In a 400cc. Pyrex beaker approximately 50 g. of columbic acid was treated with 200 cc. of concentrated sulfuric acid.[20] The beaker was covered with a watch glass and the mixture boiled for five minutes, after which it was allowed to cool to 30°. It was then transferred to a 250cc. glass-stoppered bottle and immersed in a Freas thermostat regulated to 25° ±0.01, where it remained for several days. During the interval it was shaken frequently. Then, by means of a pipet, 50cc. portions of the solution were withdrawn and centrifuged at 3000 revolutions per minute until the solutions were perfectly clear. These clear solutions were analyzed for the columbium and sulfate content by the following methods.

Methods of Analysis, (a) Cb_2O_5.—A weighed sample was carefully diluted with 200 cc. of distilled water. Ammonium hydroxide was added until the solution was faintly alkaline, the mixture heated to boiling and the precipitated columbic acid obtained by filtration. The precipitate was then washed with very dilute ammonium hydroxide till the washings failed to give a test for sulfate. The residue was dried, ignited in platinum and weighed as Cb_2O_5. The filtrate and washings were kept for the sulfate determination.

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[18] **Barr,** THIS JOURNAL, 30,1668 (1908).

[19] **Hildebrand,** *ibid.*, 30, 1672 (1908).

[20] The concentrated sulfuric acid used throughout this work was of the highest purity obtainable. It contained 95.92% of anhydrous sulfuric acid.

(b) H_2SO_4.—The combined filtrate and washings from (a) were acidified with dilute hydrochloric add and transferred quantitatively to a 500-cc. volumetric flask. The solution was then diluted, with thorough stirring, to the graduation with distilled water. To exactly 50 cc. of this solution was added an excess of a barium chloride solution to precipitate the sulfate which, after standing, was filtered, washed, dried, heated and weighed in the usual quantitative procedure. The results obtained are recorded in Table I.

TABLE I

SOLUBILITY OF COLUMBIC ACID AT 25°

Sample soln., no.	Weight of soln., g.	Cb_2O_5, g.	H_2SO_4, g.	Cb_2O_5, %	H_2SO_4, %	H_2O, by diff., %
1	8 6479	0 3044	3 213	8.34	88.06	3 60
2	3.8005	.3169	3.351	8.34	88.17	3.49
8	4.0174	.3353	3.536	8.35	88.03	3.62
4	8 6742	.3061	3.241	8.33	88 21	3 46
5	3 6396	.3043	3.206	8 36	88.09	3.55
6	3.9341	.3277	3.467	8.33	88.12	3 55
			Average	8.34	88.11	3 55

From Table I it is evident that 8.34 g. of columbium pentoxide is soluble in 100 g. of solution containing 88.11% of anhydrous sulfuric acid. The specific gravity of this solution was determined and found to be 1.85. From this we calculated that 15.43 g. of columbium pentoxide is dissolved in 100 cc. of this solution. For practical purposes, however, it may be concluded that by the above procedure approximately 15 g. of columbium pentoxide will dissolve in 100 cc. of concentrated sulfuric acid.

Similar experiments, which were carried out with columbic acid that had been prepared in the usual way except that it had been successively washed with a mixture of alcohol and water, a mixture of absolute alcohol and ether, finally anhydrous ether previously distilled over sodium and dried in a vacuum desiccator over anhydrous calcium chloride, gave approximately the same results. Analyses of the columbic acid prepared in this way gave a water content of 15.28%.

Preparation of a Solution of Columbic Acid

While determining the solubility of columbic acid in sulfuric acid the separation of a precipitate caused by hydrolysis upon dilution was noticed. When, however, care was taken to keep the solution cool during the dilution, no precipitation occurred with more extended dilution.

This led to experimentation which established the final concentration of sulfuric acid necessary to prevent precipitation from a 0.038 M solution of columbic acid when a hot solution of higher concentration of both sulfuric acid and columbic oxide was cooled in a beaker surrounded by ice and diluted. No precipitation occurred before more than three days had elapsed if the final concentration of sulfuric acid was 3 M or greater. With higher final concentrations of sulfuric acid it was possible to increase the amount of columbic acid which remained in solution. In this investigation a solution of approximately 0.025 M Cb_2O_5 was therefore employed in most of the experiments which follow because it was not deemed advisable to work with a solution which was so near the limit of solubility.

Reduction of Columbic Acid

By Chemical Means.—At the beginning of this paper a brief account of the reduction of columbic acid by a metal in mineral acids was given. After such reductions a blue solution was obtained if the acid used was dilute and a brown solution was obtained if the acid was concentrated. The exact extent of these reductions has not been definitely determined in any case and when a quantitative determination of columbium, based upon such reductions, was made an empirical rather than a stoichiometric factor was found and employed.

The colored solutions have also served to distinguish columbium from tantalum, which remains colorless in the solution. The conditions favorable to the sensitivity, however, have not been given. It was therefore considered worth while to work out the limits of the test and give the conditions most favorable.

Procedure for the Detection of Columbium in the Presence of Tantalum.—The solution to be tested was prepared according to the method described under "Preparation of a Solution of Columbic Acid." To 2 cc. of this solution in a test-tube, 1 cc. of concentrated sulfuric acid and 7 cc. of water were added. A few pieces of mossy zinc (about one gram) were next introduced and the mixture was allowed to react for five minutes. A blue solution proves the presence of columbium.

Sensitivity of the Test.—Under the above conditions it was found that the limit of the test was a 0.00032 molar columbium solution in the presence of a relatively high concentration of tantalum. When such a small quantity of columbium is present in the solution, a very pale green color is observed.

Electrolytic Reduction.—It was pointed out in the introduction that Ott[15] prepared a double salt of trivalent columbium sulfate and ammonium sulfate. This salt is not a very desirable substance from which to prepare pure solutions of trivalent columbium for several reasons. In the first place, it is difficult to free the substance from adhering sulfuric acid. Again, its ease of oxidation by air makes it impracticable to use. Besides, the presence of ammonium sulfate is undesirable in many subsequent experiments where accurate measurements are desired. It was therefore necessary to work out the conditions whereby a solution of trivalent columbium of the least complexity could be prepared which would be suitable for the various physical measurements.

A few preliminary experiments soon proved that very little reduction could be obtained at a platinum cathode. At best only a very pale blue solution was obtained. In order to secure a better reduction, it was therefore necessary to employ as a cathode a metal which possessed a higher hydrogen overvoltage. While Ott[15] used a lead cathode for reducing a solution of columbium pentachloride in concentrated sulfuric acid, it was believed that mercury, which has a much higher hydrogen overvoltage, would be better. Besides, mercury can be readily purified and it is not attacked by sulfuric acid except when the acid is both hot and very concentrated.

Reduction of Columbic Acid at a Mercury Cathode

An arrangement of the apparatus devised for the reduction of columbic acid at a mercury cathode is given in Figure 1. It consists of two wide-mouthed bottles, A and B, each of 1000cc. capacity. A, acting as the cathode, is closed with a rubber stopper pierced with five holes. Through these holes, respectively, pass a glass tube with a sealed-in platinum wire to make contact with the mercury on the bottom of the cell, a glass tube to admit hydrogen, a glass tube to act as a bridge to connect the solution in A to that in B, a glass tube leading into a bottle acting as a water seal to liberate the excess hydrogen and, finally, a narrow glass tube to deliver the reduced solution to a buret by the pressure of hydrogen.

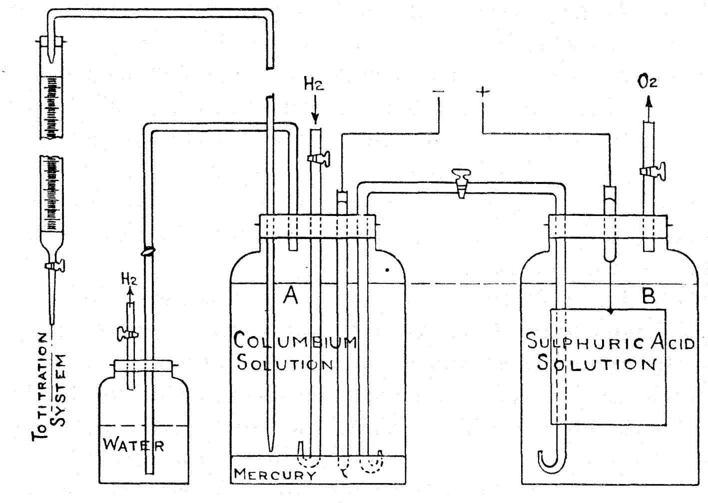

Fig. 1.—Reduction Apparatus.

The bottle B is also provided with a rubber stopper pierced by three holes through which pass, respectively, a glass tube connecting the solution in B with that in A, a glass tube to liberate any gases formed at the anode during the electrolytic reductions and a glass tube with a sealed-in platinum electrode (5 by 8 centimeters) to act as the anode. The bridge connecting A and B was made of glass tubing of 7 mm. internal diameter with openings on either end of 3 mm. diameter. The mercury used throughout this investigation was washed with nitric acid according to the method of Hildebrand.[21] It was filtered through a clean towel and was finally distilled under reduced pressure with access to air as recommended by Hulett.[22]

The bottle A, acting as the mercury cathode, held the columbic acid solution. The bottle B was filled with an equal amount of sulfuric acid of the same molarity as the solution containing the columbium. The two solutions were connected by a bridge, without plugs, filled with the sulfuric acid solution. Hydrogen from a cylinder, purified by passing it successively through alkaline permanganate, alkaline pyrogallol solution, water, cotton wool and finally through some of the same solution used in the process, was passed through the columbium solution during the reduction. The hydrogen, besides furnishing a means to exclude oxygen to which the reduced solution is sensitive, served as a stirrer.

When the arrangement of the apparatus was completed, an electric current whose current density in all reductions was three milliamperes per square centimeter was passed through the system. The progress of the reduction was determined at intervals by adding an excess of an oxygen free standard potassium permanganate solution to a test portion of the reduced solution and by titrating back with a standard ferrous sulfate solution in the following manner.

Since the reduced solution is very susceptible to the action of oxygen, the standard potassium permanganate solution was prepared with boiled distilled water and was kept under an atmosphere of hydrogen, by the pressure of which the potassium permanganate was introduced into the buret connected to the stock solution. From time to time the potassium permanganate solution was standardized against sodium oxalate which had been obtained from the Bureau of Standards. A test portion of the reduced columbium solution was obtained by allowing the pressure of hydrogen to force the solution in A into a buret, from which it was measured into a flask, previously swept by hydrogen and hermetically connected with the potassium permanganate buret, where the titration was made. In this manner the titrations were all carried out in an atmosphere of hydrogen.

The reduction was allowed to proceed until the amount of standard potassium permanganate solution required to oxidize a 25cc. portion of the reduced solution remained constant within experimental error. This point was considered to be the termination of the reduction. In the tables below are listed the data showing the progress and extent of reduc-

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[21] Hildebrand, This Journal, 31, 933 (1909).

[22] Hulett, Z. *physik. Chem.*, 33, 611 (1900).

tion of 0.025 *M* columbic acid in 3, 6 and 10 M sulfuric acid solutions, respectively.

Upon the basis that columbium is pentavalent in columbic acid and columbium pentoxide, calculations based upon the equivalents of potassium permanganate required for reoxidation to its original condition were made to establish the valence of the reduced state. In all cases whether the reduced solution was blue or brown in color the valence in the reduced form was found to be three. Percentage reduction was determined by comparing the quantity found in the trivalent state to the amount in the original solution. The limiting error in the procedure in all determinations was in the titration of the measured 25cc. portions. This did not at greatest exceed 2 parts per 1000.

TABLE II

REDUCTION AT A MERCURY CATHODE

		0.025 *M* Cb_2O_5		
25 *cc.* Sample no.	Time of reduction. hours	0.02 *M* $KMnO_4$ required, ec.	Talence of reduced from. calcd.	Columbium required, %
		3 M sulfuric acid		
1	4	22.01	...	88.16
2	6	24.66	...	98.77
3	8	24.95	3.004	99.93
4	9	24.93	3.006	99.86
5	10	24.92	3.006	99.82
6	12	24.95	3.004	99.93
Duplicate				
1	4	23.17	...	92.80
2	5	23.70	...	94.92
3	8	24.91	3.007	99.80
4	10	24.95	3.004	99.93
5	12	24.93	3.006	99.86
6	14	24.94	3.005	99.89
Triplicate				
1	4	22.54	...	90.27
2	6	24.73	...	99.04
3	8	24.94	3.005	99.89
4	10	24.91	3.007	99.80
5	12	24.93	3.006	99.86
6	14	24.94	3.005	99.89
		6 *M* sulfuric acid		
1	4	22.37	...	89.59
2	6	24.41	...	97.76
3	8	24.90	3.008	99.72
4	10	24.95	3.004	99.93
5	12	24.91	3.007	99.80
6	13	24.93	3.006	99.86

TABLE II (*Concluded*)

0.025 *M* Cb_2O_5

25 cc. Sample no.	Time of reduction, hours	0.02 M $KMnO_4$ required, cc.	Valence of reduced form. calcd.	Columbium reduced, %
Duplicate run				
1	5	23.05	...	92.31
2	6	24.62	...	98.60
3	8	24.93	3.006	99.86
4	10	24.91	3.007	99.80
5	12	24.94	3.005	99.89
		10 M sulfuric acid		
1	4	18.29	...	73.25
2	6	24.58	...	98.44
3	10	24.81	3.015	99.36
4	12	24.95	3.004	99.93
5	14	24.92	3.006	99.82
6	16	24.93	3.005	99.86
Duplicate run				
1	6	24.25	...	97.12
2	8	24.87	3.010	99.60
3	10	24 92	3.006	99.82
4	12	24.94	3.005	99.89
5	15	24.91	3.007	99.80

As a further check on the reliability of the method of reduction, the total columbium content was quantitatively determined in 25cc. samples of both the unreduced and reduced solutions—before and after reduction, respectively. The results are shown in Table III.

TABLE III

DETERMINATION OF TOTAL COLUMBIUM

Unreduced Solution			Reduced Solution	
Sample No.	Soln. cc.	Cb_2O_5, g.	Soln., cc.	Cb_2O_5, g.
1	25	0.1664	25	0.1668
2	25	.1667	25	.1663
3	25	.1666	25	.1665

To determine the total columbium content in the reduced solution, hydrogen peroxide was first added to oxidize the columbium. The resulting solution was then evaporated to at least half its volume to destroy the excess of hydrogen peroxide. Ammonium hydroxide was added to make it alkaline and the precipitated columbic acid was determined in the usual manner.

From these experiments we conclude that at a mercury cathode complete reduction to the trivalent state can be obtained, within experimental error, ranging from 99.80 to 99.96% reduction with solutions of columbium in 3 M, 6 M and 10 M sulfuric acid.

Color Changes of the Columbium Solution during Electrolytic Reduction.—In the presence of 3 M sulfuric acid the reduced solution first assumes a blue color which increases in intensity as the reduction is extended. The final solution possesses a very deep blue color and is nearly opaque. Reddish-brown solutions are obtained, however, in the presence of 6 *M* and 10 M sulfuric acid. Here also the intensity increases with the extent of the reduction. It was of interest to note that these brown solutions upon dilution became blue. Many attempts were made to isolate a solid compound of trivalent columbium from these reduced solutions but without success.

Effect of Mixing and Dilution on the Reduced Columbium Solutions.—1. Varying amounts of the reduced solutions were severally added to varying amounts of unreduced solution through which hydrogen had been previously passed to remove any traces of oxygen. The resulting mixtures, which were prepared in an atmosphere of hydrogen, were treated with a definite excess of standard potassium permanganate which was titrated back with standard ferrous sulfate. In Table IV are some of the results obtained.

TABLE IV

MIXTURE OF REDUCED AND UNREDUCED SOLUTIONS

Expt. no.	Reduced soln.,	Oxidized soln.,	0.02 *M* $KMnO_4$ req. by undil. soln., cc.	0.02 *M* $KMnO_4$ req. by dil. soln., cc.
1	25	75	24.94	24.92
2	50	50	49.88	49.83
3	75	25	74.82	74.80

Since the amount of potassium permanganate required did not vary, it was evident that no change had taken place as a result of mixing the solutions.

2. Portions of the completely reduced solutions containing 6 *M* and 10 M sulfuric acid were diluted carefully, in an atmosphere of hydrogen, with distilled water which had been previously boiled. The brown solutions became blue on dilution. A comparison of the titrations of the diluted solutions with the undiluted revealed no change in the amount of potassium permanganate required. No change of valence had occurred. The valence of the columbium in the brown solution was also three.

It seems from the foregoing experiments that the various colored solutions obtained by the electrolytic reduction of columbic acid in **3,** 6 and 10 M sulfuric acid are not due to the different valences of columbium in solution, since in each concentration of acid the trivalent state was established on the basis of the permanganate equivalents required, but to some type of complex in the strong sulfuric acid solutions which hydrolyzes or decomposes upon dilution.

Summary

1. The solubility of columbic acid, which had been prepared from the mineral Columbite according to a slightly modified procedure of Hall and

Smith, and Balke and Smith, was determined in concentrated sulfuric acid. A saturated solution was found to contain 8.34 g. of columbium pentoxide and 88.11% anhydrous sulfuric acid in 100 g. of solution.

2. The most favorable conditions were determined for preparing a stable and relatively concentrated solution of columbic acid in sulfuric acid. The solution must contain at least 3 M sulfuric acid and not more than 0.938 M Cb_2O_5 to remain stable for three days. A higher concentration of Cb_2O_5 may be obtained only when the concentration of sulfuric acid is greater than 3 M.

3. A procedure which is sensitive to 0.00032 M columbium solution was devised for the detection of small amounts of columbium in the presence of tantalum.

4. By using mercury, which has a high hydrogen overvoltage as a cathode, solutions of columbic acid containing 3, 6 and 10 M sulfuric acid were completely reduced to the trivalent state within experimental error. The apparatus devised for such reductions has been described.

This will form the basis of a volumetric method for the quantitative determination of columbium, employing a stoichiometric factor, work for which has been planned.

5. In the presence of 3 M sulfuric acid, a blue solution is obtained upon electrolytic reduction, while in 6 M and 10 M sulfuric acid, reddish-brown solutions were formed which became blue on dilution with water. These brown solutions turned blue upon dilution, indicating complex compounds rather than a different valence,

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THE DETERMINATION OF TRACES OF MERCURY.

III. THE QUANTITATIVE DETERMINATION OF MERCURY IN URINE AND FECES AND THE INFLUENCE OF MEDICATION[1]

BY N. E. SCHREIBER, TORALD SOLLMANN AND HAROLD SIMMONS BOOTH

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The method for the quantitative determination of traces of mercury described by Booth, Schreiber and Zwick[2] was intended primarily for the study of the clinical excretion of mercury. The present paper deals with its applicability to urine and feces. These may introduce complications

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[1] This research has been carried on in collaboration with Dr. H. N. Cole of The School of Medicine of Western Reserve University, as a preliminary to a comprehensive study of the absorption and elimination of mercury and mercury compounds by the human body.

The expenses have been met mainly by Lakeside Hospital, Cleveland, Ohio, and by a grant from the Therapeutic Research Committee of the Council on Pharmacy and Chemistry of the American Medical Association.

[2] Booth and Schreiber, THIS JOURNAL, 47, 2625 (1925): Booth, Schreiber and Zwick, *ibid.*, 48, 1815 (1926).

due to the presence of substances that are difficult to oxidize or to the presence of drugs which are administered to the patients. A number of these drugs were found not to interfere with the standard method, but the procedure had to be modified for iodides and large amounts of bromides, and a few drugs require such extensive modification that it appeared better to avoid their administration. The problem of the oxidation of normal urine and feces has also been satisfactorily solved.

I. Application of the Method to Normal Urine

In the previous paper[2] it was shown that the method permits the accurate determination of 5 mg. or less of mercury in a liter of water or gelatin solution with a loss of 0.01 to 0.02 mg. of mercury. To measure its availability for normal urine, small amounts of mercury were measured in the calibrated capillary buret, transferred to a 3-liter, long-necked, round-bottomed flask, dissolved in nitric acid and a liter of normal urine added. The reflux condenser was put in place and the urine oxidized, then filtered, the mercury precipitated, coagulated, filtered, decomposed, collected and measured as described in the previous paper, Table I records the result of eight analyses made after this fashion, using 0.44 to 3.26 mg. of mercury added to a liter of normal urine.

TABLE I

RESULTS ON NORMAL URINE

Mercury added, mg.	Mercury recovered, mg.	Loss, mg.	Mercury added, mg.	Mercury recovered, mg.	Loss, mg.
0.44	0.43	0.01	2.31	2.27	0.04
.98	.96	.02	2.66	2.63	.03
1.29	1.28	.01	2.98	2.97	.01
1.63	1.63	.00	3.26	3.25	.01

These results indicate that the method is applicable to the quantitative determination of small amounts of mercury in normal urines with a median loss of about 0.01 mg., that is, the same as in pure solutions of mercury salts.

II. The Effect of Standing

It is often convenient and sometimes practically necessary to keep the urines some days before analyzing. It seemed essential to make sure that this would not result in losses by gradual precipitation of the mercury on the walls of the containers. To obtain an extreme range, the mercury content was determined in the urines of several patients who were receiving mercury rubs, within twenty-four hours after the urine was voided, and again on the same urines after they had stood for six months in bottles in the refrigerator without freezing. In order to test further for the possibility of precipitation, each specimen was divided into aliquot parts. One part was measured and analyzed, while in the case of the second part the bottle was rinsed out with 10 cc. of concentrated nitric acid and this added to the specimen. The usual procedure was followed and the mercury content determined.

TABLE II

THE EFFECT OF STANDING

	After standing for 6 months	
Before standing Mercury, mg.	Without nitric acid Mercury, mg.	With nitric acid Mercury, mg.
0.35	0.34	0.35
.86	.85	.84

These results tend to show that long standing without freezing does not lessen the mercury content.

III. The Effect of Drugs on the Determination of Mercury in Urine

Before proceeding to the clinical application of the method, it appeared advisable to ascertain the possible interference of a number of drugs which are often administered to patients who are receiving mercury. Known amounts of mercury dissolved in nitric acid were therefore added to the urines of patients who were receiving these drugs, or to the normal urine to which these drugs had been added.[3] The analysis of these drugged urines showed that the intramuscular injection of neoarsphenamine, arsphenamine and of bismuth compounds, and small amounts of bromides, and the oral administration of chloral hydrate, barbital and small amounts of hexamethylenetetramine do not interfere with the standard procedure. Aromatic compounds (sodium salicylate and cinchophen) and hexamethylenetetramine if administered in large doses cannot be easily oxidized with sulfuric acid and potassium permanganate. Consequently, a considerable amount of organic matter distils over with the mercury. This can be partially prevented by washing the precipitate of mercuric sulfide and manganic hydroxide with small amounts of alcohol and ether, but the last traces of organic matter cannot be completely removed. It therefore seems better to exclude the use of these drugs from the study of mercurial medication.

Iodides, even in small amounts, and ordinary doses of bromides interfere seriously with the standard procedure. Since these drugs are often administered to patients who are receiving mercury, it was found necessary to devise a modification of the method for such cases. The interference of iodides and bromides is due partly to the formation of complex salts from which the mercury cannot be precipitated as sulfide,[4] and partly to the iodates and bromates which are formed in the oxidation. These oxidize the hydrogen sulfide and liberate free sulfur, which interferes with a complete collection of mercury.

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[3] Specimens of urine from patients who received the drugs were furnished by The City Hospital and Lakeside Hospital through the kindness of Dr H. N. Cole, Dr. J. Rauschkolb and Dr. J. Gammel.

[4] Kekulé, *Liebigs* Ann., *Suppl.*, 2, 101 (1862).

The following modification avoids these difficulties by removing the iodine or bromine. When violet or brown vapors in the course of the oxidation show that the specimen contains iodide or bromide, the oxidation is continued as described under the standard method and, when complete, the condenser is carefully rinsed and removed. Small amounts of sodium nitrite are added, the solution is gently warmed and a current of air is blown through. Usually **3** to *5* g. of sodium nitrite are sufficient to liberate the iodine or bromine and render the solution colorless. A small amount of potassium permanganate is added and the solution boiled with the reflux condenser in place. This oxidizes any nitrite to nitrate. The excess of manganese dioxide is reduced with hydrogen peroxide and the standard procedure then followed.

Table III contains the results of the analyses of medicated urines or normal urines containing drugs and to which known amounts of mercury were added.

TABLE III

THE EFFECT OF MEDICATION ON THE DETERMINATION OR MERCURY IN URINE

Medication	Administration	Dosage of drug	Mercury added, mg.	Mercury recovered, mg.	Loss . mg.	Remarks
Arsphenamine	Intramuscular	0 85 g.	3.16	3.13	0.03	
		1.35 g.	0.95	0 9 4	.01	
		1.70 g.	1.40	1.38	.02	
Barbital	Oral	0.324 g.	1.12	1.12	00	
		0 324 g.	2 23	2 21	02	
Bismuth salicylate	Intramuscular	1 04 g.	*3* 16	3 15	.01	
Bromide (sodium)	Added to urine	1 g./l.	2 08	2 07	01	Bromine vapors removed—with sodium nitrite
			4 30	4.26	.04	
Chloral hydrate	Oral	0.324 g.	2.84	2 81	.03	
			3.92	3 90	.02	
Cinchophen	Oral	0.972 g.	Under mercurial medication			Organic matter distilled over
Hexamethylenetetramine	Added to urine	1 1	0.125	0 120	005	No organic matter distilled over
		5 g./l	2 61	. .		Organic matter distilled over
Iodide (sodium)	Added to urine	0.5 g./l.	0.81	0.79	.02	Iodine vapors removed—with sodium nitrite
			5.72	5.68	.04	
Salicylate (sodium)	Oral	1.944 g.	Under mercurial medication			Organic matter distilled over

IV. The Determination of Mercury in Feces

The determination of mercury in feces presents several difficulties not encountered with the urine.[6] The usual method of oxidation with sulfuric acid and permanganate

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[5] In our earlier attempts to overcome these difficulties we enjoyed the collaboration of Dr. Karl G, **Zwick.**

could not be used. due to the formation of the insoluble sulfates which settle out and cause bumping before the destruction of the organic matter is complete. This difficulty was avoided by the use of concentrated nitric acid and permanganate, but this stronger oxidizing mixture oxidized the hydrogen sulfide, which is used to precipitate the mercuric sulfide, and caused a deposit of sulfur in the distillate. Proceeding upon the suggestion of Dr. W. F. Von Oettingen, a small spiral of 24-gage copper wire was partially oxidized in the flame, reduced with methyl alcohol and placed in the inner decomposition tube above the glass wool. This prevents the deposition of free sulfur and is now used as a matter of routine also for urine, although not always necessary.

Even with the use of strong oxidizing agents, the fats cannot be oxidized completely, but collect in a layer on the surface. Lomholt and Christiansen[6] filtered off the layer of fat and found that it retained no mercury. Our experiments[7] confirm this statement and the results in Table IV show that all of the mercury was recovered after the fat had been rejected. The Standard Method for the oxidation of feces is therefore as follows. A daily specimen (200 to 250 g.) is thinned, usually by the addition of 100 to 150 cc. of water, transferred to a 3-liter, long-necked, round-bottomed flask, 150 cc. of concentrated nitric acid is added and the mixture warmed on a steam-bath until foaming has ceased. Potassium permanganate tablets are then added, the reflux condenser is put in place and the mixture heated for about three hours longer. The flask is then transferred to a hot-plate, more permanganate added, as required, and the oxidation continued until the liquid is yellow and the fat has collected on the surface. The solution is cooled, the fat filtered off and washed with water and the filtrate oxidized with more permanganate until it is colorless. The excess manganese dioxide is reduced by adding a few drops of 50 vol. hydrogen peroxide, the excess boiled off and the solution cooled and filtered. The mercury is then precipitated, coagulated, filtered, decomposed, collected and measured as described under the Standard Method for the Determination of Mercury in Urine[a] with the addition of the copper spiral mentioned above.

In testing out this method, various amounts of mercury were measured in the calibrated capillary buret, dissolved in nitric acid, diluted to 200 cc. and precipitated as sulfide, since the mercury is eliminated as sulfide. Then 200 to 250 g. of feces were added and the Standard Procedure followed as described above. The result of five analyses made after this fashion, using amounts of mercury varying from 0.58 to 3.62 mg. are recorded in Table IV. The median loss is 0.02 mg., practically the same as with urines. The results of the oxidation with sulfuric acid are also added. The latter gave a somewhat large loss and the method was abandoned, mainly because of this inaccuracy.

TABLE IV

RESULTS ON FECES AND MERCURIC SULFIDE

A. Standard Method—Oxidation with Nitric Acid and Potassium Permanganate

Mercury added, mg.	Mercury recovered, mg.	Mercury loss, mg.
0.58	0.56	0.02
1.22	1.20	.02
2.07	2.06	.01
2.87	2.84	.03
3.62	3.58	.04

B. Oxidation with Sulfuric Acid and Potassium Permanganate (Abandoned)

Mercury added, mg.	Mercury recovered, mg.	Mercury loss, mg.
2.20	2.13	0.07
2.67	2.60	.07
3 09	2.71	.29

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[6] Lomholt and Christiansen, Biochem. Z., 81, 356 (1917).

[7] W. A. H. Naylor, Pharm. J.,4, 12, 392 (1901).

Summary

1. With normal urines the method of Booth, Schreiber and Zwick permits the quantitative determination of mercury with a loss of about 0.01 to 0.02 mg.

2. Long standing without freezing does not alter the mercury content of the urine specimens.

3. Arsphenamine, bismuth, chloral hydrate, barbital, small amounts of hexamethylenetetramine and small amounts of bromides do not interfere with the standard procedure.

4. Aromatic compounds, such as sodium salicylate, cinchophen and large amounts of hexamethylenetetramine complicate the oxidation to such a degree that it is advisable to avoid the administration of these drugs during a study of mercurial medication.

5. Iodides and large amounts of bromides interfere seriously. A modification of the method involving the addition of sodium nitrite is described which takes care of this interference.

6. The determination of mercury in the feces is best made by destroying the organic matter with potassium permanganate and concentrated nitric acid in place of sulfuric acid, with certain modifications which have been described. This determines 2 to 3 mg. of mercury in the daily stool with a loss of 0.01 to 0.04 mg. of mercury.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, THE UNIVERSITY OF MINNESOTA]

A SPECIFIC REAGENT FOR THE RAPID GRAVIMETRIC DETERMINATION OF SODIUM

BY H. H. BARBER AND I. M. KOLTHOFF

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A. Blanchetière[1] made application of Streng's reagent for the detection and precipitation of sodium as the triple salt, uranyl magnesium sodium acetate. According to his statement the precipitate has the formula $(UO_2)_3MgNa(CH_3COO)_9 \cdot 9H_2O$ and is obtained water free after drying for one-half hour at 110°.

A. Kling and A. Lassieur[2] report the results of some experiments and conclude that the method of Blanchetière gives satisfactory results. A critical survey of their data shows, however, that the relative error is -6.0 to $+3.0\%$. Crepaz[3] reports the method too inaccurate for the gravimetric determination of sodium. Recently similar results have been found by Perietzeana,[4] who states that the relative error is -3.0

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[1] Blanchetière, *Bull. soc. chim.*, [4] *33, 807* (1923).

[2] Kling and Lassieur, *Chimie et industrie, 12,1012* (1924).

[3] Crepaz, *Ann. chim. appl.*, 16,219–224 (1926); *C.* A. 20, 3144 (1926).

[4] Perietzeana, *Bull. soc. chim. România*, 9, 17–19 (1927); *C. A.*, 22, 201 (1928).

to +4.1% in solutions containing 0.23–2.3 mg. of sodium. The results which we have obtained with Blanchetière's reagent are still less satisfactory than those reported by the authors mentioned. Probably the results can be improved by using a reagent with a higher concentration of uranyl and magnesium salts than that recommended by Blanchetière. As we have obtained with a uranyl zinc acetate reagent very satisfactory results, we have not made a thorough study of the uranyl magnesium acetate reagent.

We have not been able to confirm the statement of Blanchetière that the crystalline precipitate of uranyl magnesium sodium acetate contains nine molecules of water. The precipitate we obtained lost in weight after drying for twenty hours at 110° about 0.3%. In the abstract[3] of the paper of Crepaz, it is stated that the water content of the salt is one molecule.

The uranyl zinc acetate reagent has approximately the same composition as the one recommended by Kolthoff[5] for the qualitative detection of sodium.

Preparation of Reagent

A.	Uranyl acetate ($2H_2O$)	10 g.	B.	Zinc acetate ($3H_2O$)	30 g.
	Acetic acid, 30%	6 g.		Acetic acid, 30%	3 g.
	Water to make	65 g.		Water to make	65 g.

After the salts in A and B are dissolved by warming, the solutions are mixed and allowed to stand for twenty-four hours. The precipitate of uranyl zinc sodium acetate is filtered off and a solution is obtained that is saturated with the triple salt due to the sodium contained in the chemicals which go to make up the reagent. When kept in Pyrex glass the reagent does not become turbid after long standing.

The reagents required for the determination of sodium are *(a)* uranyl zinc acetate reagent; (b) 95% ethyl alcohol saturated with uranyl zinc sodium acetate; (c) ether.

Procedure

A known amount of the weighed salt which should not contain more than 8 mg. of sodium is dissolved in **1** cc. of water. Ten cc. of the reagent is added and the whole is well mixed. The solution is allowed to stand for at least thirty minutes and is then filtered through a porous porcelain or glass filter crucible by suction. After the reagent has been removed as completely as possible, the precipitate is washed **5** to **10** times with **2** cc. of the reagent for each washing. The reagent is removed each time completely by suction. The excess is removed by washing the precipitate **5** times with **2** cc. of alcohol each time and finally by washing with ether. The amount of ether used is immaterial as the precipitate is not soluble in it. Air is now drawn through the crucible until the ether is removed. The crucible is wiped clean with a moist cloth, placed in the balance and weighed after ten minutes, or longer. The precipitate has the composition $(UO_2)_3ZnNa(CH_3COO)_9 \cdot 6H_2O$. Weight of precipitate multiplied by **0.01495** = amount of sodium.

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[5] Kolthoff, *Z. anal.* Chem., **70**, 397 (1927).

Discussion

(a) Instead of weighing the small amount of sodium salt given in the procedure, we always proceeded in such a way that a known amount of sodium salt was made up with water to a special weight.

(b) The ratio between the volume of the solution of the sodium salt and the reagent must be 1 to 10 or larger than 10. In case 2 cc. of aqueous solution is used, 20 cc. of the reagent should be added.

(c) The precipitation of the triple salt is a time reaction. Satisfactory results are obtained by collecting the precipitate after standing for one-half hour. Longer standing has no influence on the results.

(d) The solubility of the precipitate increases very much with rise in temperature; consequently, the temperature of the solution at time of filtration should be approximately the same as that at which the reagent was filtered from the triple salt.

(e) In most of our experiments we washed with pure 95% alcohol. The results obtained were somewhat too low. The error amounted to about −0.5%. This is due to the slight solubility of the precipitate in 95% alcohol, The solubility is about 0.5 mg. per cc. at room temperature (22°); therefore we recommend that the alcohol be saturated with the precipitate. Especially in the determination of traces of sodium the use of this wash alcohol, saturated with the precipitate, is of importance. In cases where the amount of sodium is about 4 mg., or higher, it is practically immaterial whether the alcohol is saturated with the precipitate, or not. It may be remarked here that the solubility of the precipitate in absolute alcohol is distinctly higher than in 95%, about 2 mg. per cc. in absolute.

Properties of Uranyl Zinc Sodium Acetate.—The salt is nicely crystalline (tetrahedrons) and is readily soluble in water. The solubility is suppressed by an excess of the reagent. In order to get a quantitative precipitation of the sodium, an appreciable excess of the reagent must be used. We did not determine the solubility of the compound in the reagent as the latter was saturated with the triple salt. In order to be sure that the compound was insoluble in the reagent, we washed 300 mg. of the precipitate with 50 cc. of the reagent. No loss in weight was noted. By the addition of an excess of alcohol, it is possible to precipitate the dissolved sodium compound from the reagent. This shows the presence of dissolved sodium triple salt in the reagent.

In the first experiments we tried to weigh the precipitate in the anhydrous form and dried it for this purpose between 100 and 140°. These experiments showed that the water of crystallization is held very tenaciously, and that it was practically impossible to remove this water without decomposing the salt. On drying between 100 and 140° the weight decreased continuously, as may be seen from some of the following experimental figures.

Behavior or the Triple Salt on Drying

Calcd. % for $6H_2O$	Loss in weight after drying (average), %				
	1 hr., 100°	14 hrs., 110°	32 hrs., 110°	1 hr., 125°	6 hrs., 140°
7.03	0.25	5.87	8.05	7.33	9 81

In order to he sure that the precipitate contained six molecules of water we tried to remove the latter at lower temperatures by drying in a vacuum. After drying for two hours between 90 and 100° at 30 mm. pressure, the salt lost 6.94 to 7.03% of water. The theoretical amount for six molecules is 7.03%. Another two hours' drying under the same conditions caused only a slight decrease in weight, a few hundredths of one per cent.

The hydrated salt is very stable at room temperatures. It does not lose its water after remaining over concentrated sulfuric acid or anhydrous calcium chloride for several days. For these reasons it is advantageous to weigh the triple salt in the form obtained at room temperature. This procedure, moreover, shortens the time of analysis.

Experimental

As the precipitate contains only 1.495% of sodium, even small amounts of the latter give relatively large amounts of the salt. One mg. of sodium will give 66.88 mg. of the triple salt; consequently, traces of sodium can be determined by the described method.

The sodium chloride used in the experiments was highly purified and thoroughly dried at 600°. No impurities could be detected in the salt.

One cc. of a standard sodium chloride solution was pipetted and weighed accurately. In this manner the weighing error of the salt was negligibly small.

Results

In Table I the results are reported which were obtained by washing out the reagent with pure 95% alcohol.

Table I

Determination of Sodium as Triple Salt—1Cc. Solution + 10Cc. Reagent

Amount of NaCl taken, g.	Time of standing before filtering, hrs.	Weight of ppt., g.	Amount of NaCl found, g.	Error, %
0.01255	50	0.3300	0.01254	-0.1
.01263	50	.3307	.01257	- .5
.01127	50	.2957	.01124	- .3
.01171	50	.3084	.01173	+ .1
.01215	52	.3176	.01207	- .7
.01173	52	.3055	.01161	-1.0
.01185	47	.3110	.01182	-0.3
.01161	47	.3057	.01158	- .3
.01317	47	.3452	.01312	- .4
.01251	47	.3299	.01254	+ .3
.01258	$^1/_2$	.3295	.01252	- .5
.01277	$2^3/_4$	.3353	.01274	- .3
.01296	$^2/_3$	.3400	.01292	- .3

TABLE I (*Concluded*)

Amount of NaCl taken, g.	Time of standing before filtering, hrs.	Weight of ppt., g.	Amount of NaCl found, g.	Error, %
01320	1/3	.3469	.01318	− .2
.005977	1	.1560	.005928	− .9
.003708	5/6	.0970	.003686	− .6
.02344	24	.6104	.02320	− 1.0
.02600	24	.6767	.02571	− 1.1

In Table II the experiments are given in which the wash alcohol was saturated with the precipitate.

TABLE II

PRECIPITATE WASHED WITH ALCOHOL SATURATED WITH PRECIPITATE

Amount of NaCl taken, g.	Time of standing before filtering	Weight of ppt., g.	Amount of NaCl found, g.	Error. %
0.01411	2 hours	0.3721	0.01414	+0.2
.01437	2 hours	.3797	.01443	+ .4
.01914	45 minutes	.4940	.01921	+ .3
.01164	50 minutes	.3068	.01165	+ .1
.01426	37 minutes	.3752	.01426	.0
.01589	3 hours	.4172	.01586	− .1
.01456	1 hour	.3860	.01467	+ .7
.01237	30 minutes	.3263	.01240	+ .3
.01419	40 minutes	.3726	.01416	− .2
.002854	2 hours	.0753	.002861	+ .3
.003121	45 minutes	.0822	.003123	+ .1
.006075	30 minutes	.1600	.006080	+ .1

From these analyses it may be concluded that the method gives results accurate to about 0.5%.

Influence of Other Salts

Influence of Potassium.—As the separation of sodium and potassium is of very great practical importance, we made a special study on this point. Kolthoff[5] stated that solutions which contained more than 50 mg. of potassium per cc. gave a precipitate with the reagent; therefore we could expect that large amounts of potassium would interfere with the determination of sodium. Our results are shown in the following table.

TABLE III

INFLUENCE OF POTASSIUM—1 CC. SOLUTION + 10 CC. REAGENT

NaCl taken, g.	KCl taken, mg.	Time of standing before filtering, hrs.	Weight of ppt., g.	NaCl calcd. from ppt. obtained, g.	Error. %
0.01362	24.3	0.5	0.3576	0.01360	− 0.2
.01254	48.7	15	.3286	.01249	− .4
.01177	68.3	16	.3149	.01197	+2
.01311	69.2	20	.3469	.01318	+0.5
.01214	73.3	47	.3416	.01298	+7
.01223	99.0	47	.3502	.01331	+8
.01189	123	47	.3267	.01213	+2

It follows from this table that good results are obtained if less than 50 mg. of potassium chloride per cc. of solution are present. When the potassium chloride content is between 50 and 150 mg. per cc. of solution, too high results are obtained. This is due to the potassium triple salt crystallizing out with the uranyl zinc sodium acetate. On the other hand we have found that when more than 150 mg. of potassium chloride per cc. of solution with 10 cc. of reagent is present, much too low results are obtained. This is due to the fact that the potassium takes much of the reagent for its precipitation as the triple salt and there is not enough of the reagent left for the quantitative precipitation of the sodium; therefore, a part of the latter goes into the filtrate. This is shown by the following experiments.

TABLE IV

INFLUENCE OF POTASSIUM

NaCl taken, g.	KCl taken, mg.	Weight of ppt., g.	NaCl calcd. from ppt. obtained, g.	Reagent used, cc.
0.01219	255	0.2266	0.008611	10
.01242	320	.1795	.006821	10
.01202	400	.3134	.01191	50

For every 50 mg. of potassium chloride per cc. of solution, 10 cc. of the reagent should be added. For cases where the ratio of sodium to potassium is very unfavorable, the potassium may be removed as potassium perchlorate. Details will be given later.

It may be remarked here that if a large amount of potassium is present as sulfate, the method does not give as good results as when the potassium is present as chloride; potassium sulfate is precipitated by the reagent. As barium does not interfere with the sodium determination, the sulfate ions can be easily removed as barium sulfate.

Influence of Ammonium Salts.—Even large amounts of ammonium salts do not interfere, as may be seen from the following results.

TABLE V

INFLUENCE OF AMMONIUM SALTS—1 CC. OF SOLUTION + 10 CC. OF REAGENT

NaCl taken, g.	Ammonium salt taken, g.	Weight of ppt., g.	NaCl found, g.	Error, %
0.01120	1.015 Cl^-	0.2928	0.01113	−0.6
.01174	1.004 SO_4^{--}	.3092	.01175	+ .1
.01358	1.036 NO_3^-	.3589	.01364	+ .4

Influence of Lithium.—Lithium triple salt is still less soluble than the corresponding potassium compound. Experiments are being made to get a good separation between sodium and lithium. Probably the alcohol method may be applied for the extraction of lithium chloride from a mixture of the alkali chlorides.

Influence of Strontium.—Too high results are obtained when strontium is present. If strontium salts are added to the reagent, a fine, white precipitate separates, probably strontium acetate. A continued study on this point is being made.

Influence of Barium, Calcium and Magnesium.—In the concentrations investigated, as given in Table VI, these alkaline earth metals do not have an interfering action, as may be seen from the following results.

TABLE VI

INFLUENCE OF BARIUM, CALCIUM OR MAGNESIUM—1 CC. OF SOLUTION + 10 CC. OF REAGENT

NaCl taken, g.	Alkaline earth salt taken, mg.	Weight of ppt., g.	NaCl found, g.	Error, %
0.01304	178 $MgSO_4$	0.3417	0.01299	– 0.4
.01464	825 $CaCl_2\cdot6H_2O$	.3874	.01472	+ .5
.01324	200 $Ba(NO_3)_2$	.3464	.01316	– .6

We may mention here that the reagent contains, usually, a little sulfate as an impurity; therefore, if barium is present a little barium salt should be added to the reagent so that the sulfate ions are removed as barium sulfate; otherwise too high results will be obtained.

The sodium determination gives such satisfactory results that the method has already been applied for the quantitative determination of sodium in the commercial salts of the alkaline earth metals.

As concerns the influence of other cations, we may state as a matter of fact that zinc does not influence the results of the sodium determination, and that it may be expected that other cations will not interfere. This point is still under investigation. We believe that the method described will be found to be quite specific for the determination of sodium in the presence of most of the other cations.

From the anions the phosphate ion has an interfering action as it precipitates as uranyl phosphate. Probably the phosphate can be removed in this form with the reagent before the sodium is precipitated.

Large amounts of organic acids, such as oxalic and tartaric, interfere. We plan to make a more systematic investigation on the applicability of the method in many different cases.

The results so far obtained are important enough to expect a general application of this specific and fairly accurate sodium determination.

Summary

1. A procedure is described for precipitating and weighing sodium as $(UO_2)_3ZnNa(CH_3COO)_9\cdot6H_2O$.
2. The influence of some cations and anions has been mentioned.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE POTENTIOMETRIC DETERMINATION OF GALLIUM

BY H. DARWIN KIRSCHMAN AND J. B. RAMSEY

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Introduction

The methods of determining gallium so far described in the literature are based on its precipitation as the hydroxide and the subsequent ignition to the oxide. Slightly different procedures for doing this have been described by Porter and Browning[1] and by Dennis and Bridgman.[2]

To facilitate further study of the chemistry of gallium, an accurate volumetric method is desired.

Since gallium is known to form a slightly soluble ferrocyanide and a soluble ferricyanide, the system might be expected to lend itself to the method of electrometric titration which has been worked out for the related elements, zinc, cadmium, and more recently indium.[3,4]

The results of the investigation described in this paper show that the method is applicable to gallium. The composition of the insoluble ferrocyanide formed has been determined and the conditions for obtaining accurate results have been studied.

Description of the Apparatus

The apparatus used consisted of (1) a motor-driven stirrer; (2) a 1 N potassium chloride–calomel reference half-cell; (3) an oxidation-reduction electrode made by fusing 1 cm. of platinum wire, 0.05 cm. in diameter, into the end of a small glass tube; (4) a certified buret; and (5) a Leeds and Northrup student potentiometer with a Leeds and Northrup galvanometer of 2.84 megohms sensitivity. A 1-liter beaker was found to be a convenient titration vessel.

Preparation of the Materials

Metallic gallium obtained originally from the Bartlesville Zinc Company of Bartlesville, Oklahoma, was the substance used in the preparation of all solutions of gallium salts. The metal was dissolved in 12 *N* hydrochloric acid and to increase the rate of solution, which is slow, a piece of platinum foil was kept in contact with the metal The resulting solution was diluted with about 250 cc. of water and the gallium precipitated as the hydroxide with a slight excess of ammonia. After heating the solution to boiling for a few minutes to coagulate the precipitate, the hydroxide was filtered off and washed free from all but a trace of chlorides. Later work showed that the gallium was not completely precipitated. Our results indicated that the hydroxide is much more

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[1] Porter and Browning, THIS JOURNAL, 43, 111 (1921); *ibid.*, 41, 1491 (1919).

[2] Dennis and Bridgman, *ibid.*, 40, 1531 (1918).

[3] Bray and Kirschman, *ibid.*, 49, 2739 (1927).

[4] Müller and Gabler, *Z. anal. Chem.*, 62, 29 (1923).

soluble in dilute ammonia than would be inferred from the literature. The precipitate of hydroxide was then dissolved in a measured amount of C. P. 12 N hydrochloric acid and diluted to approximately **0.08 molal** in gallium chloride.

The potassium ferrocyanide and potassium ferricyanide used were of the standard C. P. quality. The solutions of potassium ferrocyanide, containing **1** g. of ferricyanide per liter, were made up in brown, glass stoppered bottles and kept in the dark when not in use. The solutions were standardized against metallic zinc by the potentiometric method.[5]

The following series of values, **0.05589; 0.05581; 0.05583,** obtained for the molality of one of the ferrocyanide solutions shows the reproducibility of the method.

Results of the Titration Experiments

Preliminary experiments showed that solutions of gallium chloride, titrated potentiometrically with potassium ferrocyanide, give curves similar in form to those obtained in the titration of zinc or indium.[3] The results of titrations under varying conditions are shown in Table I.

TABLE I

RESULTS OF TITRATIONS OF GALLIUM CHLORIDE SOLUTIONS WITH POTASSIUM FERROCYANIDE

Expt.	Stock soln.	*Wt.* of $GaCl_3$ *solo., g.*	Vol *of* $K_4Fe(CN)_6$, *cc.*	*Ratio*	*Temp.*	*Total* vol., *cc.*	Aridity, *N*
1	A	10.29	14.10	1.370	Room	450	0.025
2[a]		10.33	...	...	Room	450	.125
3		10.32	14.16	1.372	75"	400	.03
4		10.34	14.20	1.373	Room	400	.03
ti		10.37	14.22	1.371	Room	325	.03
7[b]		10.44	...	...	Room	425	..
8		10.34	14.21	1.374	Room	425	.01
1	B	10.12	11.32	1 118	40°	350	005
2		21.26	22.68	1.119	40°	800	.005
3		20.21	22.61	1 119	Room	800	.005
4		20.23	22.77	1.125	60°	800	.005
5		20.21	22.68	1.122	40°	400	.01
6		10.13	11.34	1.120	60°	800	.003
7[c]		20.24	...	...	75°	800	.005

[a] Five ec. of 12 *N* HCI was added.

[b] Ammonia added till neutral.

[c] Decomposition observed.

These three runs gave curves from which the end-points could not be satisfactorily determined.

During the titration, equilibrium is substantially attained in from *3* to 5 minutes except in the immediate vicinity of the end-point, where the voltage is changing most rapidly. The volume of ferrocyanide solution used was obtained by determining the inflection point of the curve which resulted on plotting voltage against *cc.* of ferrocyanide solution added.

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[5] Bichowsky, *J. Ind. and Eng. Chem*, *9*, **668 (1917); Müller, Z.** *anorg. Chem., 128, 126* **(1923);** Treadwell and Chevert, *Helv. Chim. Acta*, **6, 550 (1923);** Verzijl and Kolthoff, Rec. *trav. chim., 43,* **389 (1924).**

The end-points were determined independently by the two authors from the titration data and differed on the average by **0.018** cc. in the 11 observations given in Table I.

In all experiments the ferrocyanide was added to the gallium chloride solution. Voltages were read to one millivolt as soon as equilibrium was substantially attained after each addition. At the beginning of the titration and up to within two or three cubic centimeters of the end-point, the ferrocyanide was allowed to run from the buret fairly rapidly. The voltage gradually rises with the addition of the ferrocyanide solution to about **0.60** volt and then remains practically constant until within a few cubic centimeters of the end-point after which a gradual decrease of potential occurs. Thereafter additions of 0.5 cc. were made and finally of **0.10** cc. as the end-point was more closely approached.

The shape of the titration curves obtained is indicative of the suitability of experimental conditions. An increase in concentration of hydrochloric acid was found to decrease the drop in potential at the end-point making this drop more gradual and therefore the inflection point less accurately determinable. The solutions of gallium chloride having the lowest acid concentration gave the most satisfactory curves. The effect of neutral salts was essentially the same as that of acid.

The curves resulting from the experiments at room temperature, 40 and 60° were similar and the corresponding ratios are the same as shown in Col. 5 of Table I. At 75° appreciable decomposition occurred, as evidenced by the blue color which developed during the titration, and the curves obtained were less satisfactory. Since equilibrium was not attained as rapidly at room temperature as at the higher temperatures, 40° was selected for subsequent titrations. It was found desirable to maintain the temperature within two degrees of that adopted because of the large temperature coefficient of the cell.

Three determinations employing an approximately 0.05 molal potassium ferrocyanide were made. Weighed amounts of the ferricyanide were added to the titration vessel. A sixteen-fold variation in the amount of ferricyanide present at the end-point produced no marked change in the type of curve obtained. We conclude that the amount of added ferricyanide can vary within rather wide limits, and since the presence of ferricyanide has been shown to prevent the decomposition of the ferrocyanide[6] it is preferable to add it with the ferrocyanide.

Composition of the Precipitate

The ratio of the gallium to the ferrocyanide in the precipitate obtained was determined by two independent methods, one employing metallic gallium as a reference substance and the other employing the oxide.

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[6] Kolthoff, *Rec. trav. chim.*, **43**, **380** (1924).

The gallium was prepared by electrodeposition[7] on a rotating platinum cathode from a solution of gallium sulfate to which sufficient ammonia had been added to produce a slight permanent precipitate of the hydroxide. The cathode coated with the gallium metal was washed, dried in an oven at 110° and weighed. The sample taken for a titration was obtained by treating the electrode with 1–2 cc. of 12 N hydrochloric acid, washing it, drying and weighing again. The gallium dissolves less readily than does indium and the solution was heated to hasten the reaction. This solution was diluted to 800 cc. and the titration carried out at 40°. The results of these titrations are shown in Table II.

TABLE II

TITRATION OF METALLIC GALLIUM AGAINST POTASSIUM FERROCYANIDE

Gallium metal, mg.	Milliatoms of gallium	$K_4Fe(CN)_6$, ml.	Millimoles of $K_4Fe(CN)_6$	Ratio $Ga:Fe(CN)_6$
33.0	0.473	6 28	0.351	1.348
42.9	.615	8.45	.472	1.304
113.3	1 625	21.71	1 212	1 340
57.9	0 830	11.19	0.625	**1.329**
81 8	1.173	16.04	896	1.310
68.3	0 980	13.18	.736	1.331
			Average	1.327

The procedure adopted in the precipitation of the gallium as hydroxide and its subsequent ignition to the oxide was essentially that recommended by Porter and Browning.' Ammonium acid sulfite was used as the precipitating agent in a neutral or slightly acid solution. A test was made for complete precipitation by evaporating the filtrate to approximately 50 cc., adding 10 cc. more of the ammonium acid sulfite solution and boiling for a few minutes. No precipitate was formed and only a very faint turbidity was observed on the addition of potassium ferrocyanide to the resulting solution.

The weights of oxide obtained from two equal portions (10.10 g.) of the gallium chloride solution were 0.0804 g. and 0.0809 g. The weights remained constant even after four hours' heating at a temperature of approximately 800°. In this respect it differs from indium oxide which has been found to lose weight when heated to this temperature.[3] The gallium oxide was not markedly hygroscopic after this treatment.[2] The average weight of oxide, 0.08065 g., corresponds to 0.8605 milliatom of gallium. The number of millimoles of ferrocyanide corresponding to 10.10 g. of the stock solution as calculated from the average of four titrations was 0.6432. From these data the ratio of gallium to the ferrocyanide in the precipitate is seen to be **1.337.**

From these results the ratio of gallium to ferrocyanide is clearly **1.333,**

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[7] Fogg and James, THIS JOURNAL, 41, 947 (1919); Richards and Boyer, *ibid.*, 41, 133 (1919); Dennis and Bridgman, *ibid.*, 40, 1537 (1918).

which corresponds to the formula $Ga_4(Fe(CN)_6)_3$ for the precipitate. The precipitate is not of a complex nature and therefore differs from the ferrocyanide of zinc and indium. The determination of this ratio makes it possible to use ferrocyanide solutions, standardized against metallic zinc, for the determination of gallium.

Summary

A method of analyzing gallium chloride solutions by titrating with standard potassium ferrocyanide solution in the presence of ferricyanide and determining the end-point potentiometrically has been described. The accuracy is estimated at two or three tenths of one per cent.

The ferrocyanide precipitate formed under the conditions described has been shown by two independent methods to have the formula $Ga_4(Fe(CN)_6)_3$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF STANFORD UNIVERSITY]

SOAPS AS COLLOIDAL ELECTROLYTES

BY JAMES W. MCBAIN

RECEIVED MARCH 26, 1928 PUBLISHED JUNE 5, 1928

It is well known that members of the large class of substances exemplified by the family of soaps exhibit in solution only moderate osmotic effect or activity, whereas their conductivity is excellent. So much is this the case, that often the whole activity seems to be ascribable to the concentration of one simple ion as measured by any of the ordinary methods leaving the carrier of the opposite charges to be explained as highly conducting colloidal particles or ionic micelles.[1] It is clear that this interpretation necessitates a broader interpretation of the electrolytic dissociation theory than that which is currently being attempted for electrolytes in aqueous solution. Linderstrøm-Lang[2] has tried to fit the data for soap solutions to the Procustes' bed of the 100% ionization theory on the assumption that soap solutions are completely dissociated into ordinary sodium or potassium ions and simple univalent fatty ions. It is the object of this note to point out that this cannot be done without deliberately ignoring too many facts.

It is perfectly possible, by means of ad *hoc* assumptions, to regard almost any substance, whose solution conducts, from the standpoint of 100%

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[1] References to previous papers from the Bristol and Stanford Laboratories may be found in the following: McBain and Buckingham, J. *Chem. Soc.*, 1927, 2679–2689; McBain, Willavoys and Heighington, *ibid.*, 1927, 2689–2699; McBain, Chap. 16, pp. 410–429 of "Colloidal Behaviour," Vol. I by Bogue; see also Salmon, THIS JOURNAL, 42, 426–460 (1920); other similar references in Linderstrøm-Lang, ref. 2.

[2] Linderstrøm-Lang, *Compt. rend. Lab. Carlsberg*, *16*, No 6, 1-47 (1926).

ionization, provided that one takes into account only osmotic or activity data. This is what is done by Linderstrøm-Lang, apart from a passing qualitative reference to the viscosity of soap solutions. He himself points out that it is going to be difficult to explain the conductivity data but shelves this problem on the ground that conductivity data are no longer thought to be understood.

The picture given by Linderstrøm-Lang[2] is as follows. In a 1 N solution of sodium palmitate the length of each palmitate ion (25 Å.) is more than twice as great as the average distance between the sodium ions (10 Å.) and of course the negative charges are carried only on one end of the long writhing fatty ions. Hence the solution is a tangle something like cotton waste and there will be strong attractive forces between the paraffin chains, minimized only by the sodium ions interspersed amongst them. The tangle might explain a high viscosity[3] and its screening action in the "abnormally low" osmotic activity.

Linderstrøm-Lang rightly remarks that osmotic experiments alone cannot prove the presence of micelles or colloidal particles. The converse is equally true, but he prefers not to assume their formation. He is influenced by the observation that soap solutions are "absolutely as clear as water and show no trace of Tyndall effect." However it must be pointed out that there is no optical evidence for the existence of a large number of colloids. It does not appear to be generally appreciated how many colloidal particles are invisible in the ultramicroscope. Further, Dr. H. Harris showed in the Bristol Laboratory that all the colloidal jellies which have been noted in the literature, such as soap, magnesium arsenate, ferric hydroxide, dibenzoylcystine, barium malonate, lithium urate, if prepared with sufficient care, are invisible in the ultramicroscope. Probably no one would care to conclude that these are all in true molecular solution.

Four kinds of data will here be cited which are directly at variance with the conception of a 100% dissociation into simple ions; namely, ultrafiltration, migration, viscosity and hydrolysis.

Ultrafiltration experiments by Dr. Jenkins and the writer[4] and subsequent (unpublished) data have shown that where the comparison between the quantitative data for activity and conductivity indicated the presence of crystalloidal soap only, the whole of the soap solution passed through dense ultrafilters. On the other hand, where such data on our interpreta-

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[3] Linderstrøm-Lang and the writer agree in thinking that the high viscosity observed in certain soap solutions cannot be ascribed to "hydration" but must have a mechanical origin. The writer has developed a general hypothesis for high viscosity on the basis of the immobilization of large tracts of solvent or solution through the chance intermeshing of ramifying aggregates of colloidal particles, *J. Phys. Chem*, 30, 239–247 (1926); *Nature*, 120, 362 (1927).

[4] McBain and Jenkins, J. *Chem. Soc.*, 121, 2325–2344 (1922).

tion indicate complete formation of colloid, the whole of the soap may be filtered off by a moderately dense ultrafilter. In intermediate cases where the data showed definite proportions of both crystalloid and colloid, approximately that proportion corresponding to the crystalloid passes through the ultrafilter. It is difficult to avoid the conclusion that the colloid consists of particles and not of the simple ions and molecules to which the ultrafilter is completely permeable. Incidentally it may be mentioned that a very coarse ultrafilter suffices to filter off much of the predicted neutral colloidal particles in a solution of the highest soaps such as sodium oleate. Further it should be pointed out that there is no difference in kind but only in degree in all hitherto observed properties of all soap solutions in the cold and at high temperatures. Colloidal particles persist into much lower concentrations at room temperature. This statement, of course, refers to solutions only and not to systems from which the soap has crystallized out (for example curds).

Migration data have been obtained for various soap solutions by Bowden[6] and Quick[6] in the writer's laboratory and a comprehensive study of sodium oleate has been published by Miss Laing.[7] The salient fact for the present purpose is that in solutions containing colloid the migration number of the fatty radical is greater than unity; that is, the sodium or potassium is moving to the anode—in the opposite direction from that of real sodium and potassium ions. This we explain, quantitatively, as being due to the sodium or potassium carried in the undissociated colloid.

Linderstrøm-Lang casually mentioned viscosity; but it would be almost impossible to explain why the viscosity of the soap solution may vary a thousand-fold with change of temperature alone, if the constituents are only those assumed by him. A further problem would be to try to explain why adding to his tangle a small amount of a salt or base like sodium chloride or hydroxide lowers the viscosity, and still further why a greater addition of almost any soluble salt can thereupon increase the viscosity fifty-fold, and still further addition lowers the viscosity to a small fraction of this again—all in homogeneous solution, and with only simple univalent ions present!

The hydrolysis alkalinity of a simple electrolyte of the type of sodium acetate increases steadily with concentration in accordance with the universal principle of mass action. Not so in soap solutions; here the concentration of hydroxyl ions increases when soap is added to water, passes through a maximum and diminishes again in the more concentrated solution because the hydrolyzable simple fatty ion is being replaced by ionic micelle.

[5] McBain and Bowden, *J. Chem. Soc.*, 123, 2417 2430 (1923).

[6] Quick, *ibid.*, 127, 1401–1411 (1925).

[7] Laing, *J. Phys. Chem.*, 28, 673–705 (1924).

Even conductivity should not be completely ignored, since there is no vast discrepancy between the two extreme oversimplified theories, that of Arrhenius and the 100% hypotheses.

All the known data of soap solutions may be interpreted in terms of the writer's theory of colloidal electrolytes, and no other hypothesis has attempted this. On the whole it seems probable, especially from the data on ultrafiltration and migration, that soap solutions contain both neutral colloid and ionic micelle. In an address to the Fourth National Colloid Symposium[8] the writer advanced the view that reversible colloids such as soap are truly (that is, thermodynamically) stable in the colloid state, inasmuch as the colloidal particles are formed spontaneously from crystals and crystalloidal molecules and ions. It is suggested that this necessitates a structure of the micelle which exposes the active groups of every molecule or ion. Such a stable structure is exemplified by a monomolecular film of palmitic acid on water, or by the conception of the ionic micelle as a radiating ball of ions resembling ten eels tied together by their tails, the charges being on the outside extremities. Likewise a possible structure for the neutral micelle is a double layer of parallel molecules of sodium palmitate with the carboxylate groups and hydration on the outer surfaces. From the standpoint of conductivity, osmotic activity and electrolytic migration, all these can be treated as special cases of a general dissociation theory. The perfect theory would include not only strong and weak electrolytes but even the slightly charged colloids such as ferric hydroxide, gold or the neutral micelles of soap, and it must also embrace the striking phenomena common in non-aqueous solutions.

Finally, the question as to the effect of the presence of ionic micelle upon the observed activity of univalent ions needs to be dealt with. If the ionic micelle is, for example, decavalent, the usual rules of ionic strength might lead us to expect that any monovalent ions in the solution would show abnormally low activity. This might be taken as partly accounting for the low activity of soap solutions, but only after postulating the existence of the polyvalent ionic micelles, the very point in question. Instead of speculating, we may turn to the published facts.[6,9] For example, when potassium chloride is added to a solution of potassium laurate at 18°, the lowering of vapor pressure or of freezing point is greater than that which the same amount of potassium chloride produces in water, and is thus too large instead of being greatly deficient. The migration data prove that in such mixed solutions the salt has diminished the amount of current carried by the soap (lessened its degree of dissociation) and we conclude that, since the osmotic effect exhibited by the salt is enhanced

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[8] McBain, "Fourth Colloid Symposium Monograph," Chemical Catalog Co., New York, 1926, pp. 7–18.

[9] McBain, Taylor and Laing, *J. Chem. Soc.*, 121, 621–633 (1922).

instead of being masked in the presence of ionic micelles, the soap is heavily hydrated, obtaining a value for the hydration in accord with other lines of inference. At 90° the additional lowering of vapor pressure caused in a solution of sodium palmitate on the addition of electrolyte, is between 75 and 80% of that which the electrolyte alone would produce in water, instead of being only the very small fraction expected on the basis of the 100% ionization theory in the presence of a decavalent ion. Soap appears to be far less hydrated at high temperatures and the observed lowering of vapor pressure is almost that which would be expected from the mutual influence of two univalent salts on each other's dissociation.

The data therefore show that the ionic micelle does not in fact conform to the rule of ionic strength, and there is an obvious explanation. In an ordinary polyvalent ion the charges carried by any one ion are necessarily close together, and may be regarded as almost coincident in comparison with the distances separating different ions from each other throughout the solution. An ionic micelle is very different, since the charges are held far apart whether in a protein or a soap micelle. If the ionic micelle of sodium palmitate has the structure indicated above and if the hydrocarbon chains were stretched to their full length, its diameter would be about 50 Å. and the distance between charges on the same ionic micelle would be over 20 Å. That is, the charges on any one such ionic micelle would be twice as far apart as the average distance of chlorine ions from each other in a normal solution of sodium chloride. It is more likely that the hydrocarbon chains do not stretch out so far, but even so the distance between neighboring charges will still be over 10 Å. Hence the ionic micelle does not represent a high local condensation of electric charge and therefore does not exert the expected effect upon activity.

Summary

1. It is shown that the attempt to describe soap solutions on the basis of dissociation into simple monovalent ions only, instead of colloidal micelles, cannot be carried through without ignoring the ascertained facts of ultrafiltration, migration and viscosity as well as conductivity.

2. The ionic micelle is an exception to the rule of ionic strength because of the large distance between the charges carried on a single ionic micelle in contrast to the proximity of the charges on an ordinary polyvalent ion.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

A STUDY OF THE OXIDATION OF SOME DICARBOXYLIC ACIDS BY HYDROGEN PEROXIDE IN THE PRESENCE OF CERTAIN CATALYSTS[1]

BY JAMBS H. WALTON AND DONALD P. GRAHAM

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In an investigation by Christensen and the senior author[2] of this paper, it was shown that ethanol is completely oxidized to acetic acid by hydrogen peroxide in the presence of iron salts (Fenton's reagent). The effect of temperature and of hydrogen ion concentration as well as concentrations of reactants and catalysts were investigated at that time. The present paper is a continuation of the above mentioned work, and deals with the oxidation of certain dicarboxylic acids of the paraffin series.

Methods.—The solutions to be used were placed in a thermostat and allowed to come to the temperature at which the reaction was to be studied. Known quantities of the catalyst were then pipetted into 100 cc. volumetric flasks, together with the acid under investigation and the requisite amount of hydrogen peroxide. The flasks were then filled to the mark with distilled water at the temperature of the reaction and placed in a thermostat. The progress of the reaction was followed by titration of samples withdrawn at definite time intervals. The acid strength was followed by titration with standard alkali, while a permanganate titration furnished an index of the concentration of the hydrogen peroxide. The dicarboxylic acids so studied were oxalic, succinic, malic, lactic and tartaric acids, with iron and copper salts as catalysts. Similar studies were made on glycerol, formic acid and ethylene glycol.

Results

Oxalic Acid.—The oxidation of oxalic acid by comparatively concentrated solutions of hydrogen peroxide, about 10 per cent. by weight, was studied by Hatcher,[3] and Hatcher and Holden,[4] who investigated the effect of acids on the reaction in the absence of catalysts. No appreciable oxidation of the oxalic acid by solutions of hydrogen peroxide of a concentration of less than 6% was observed. From these results and the fact that oxalic acid is rather easily oxidized by a number of the more common oxidizing agents, it was expected that it would be easily oxidized by dilute solutions of hydrogen peroxide in the presence of a

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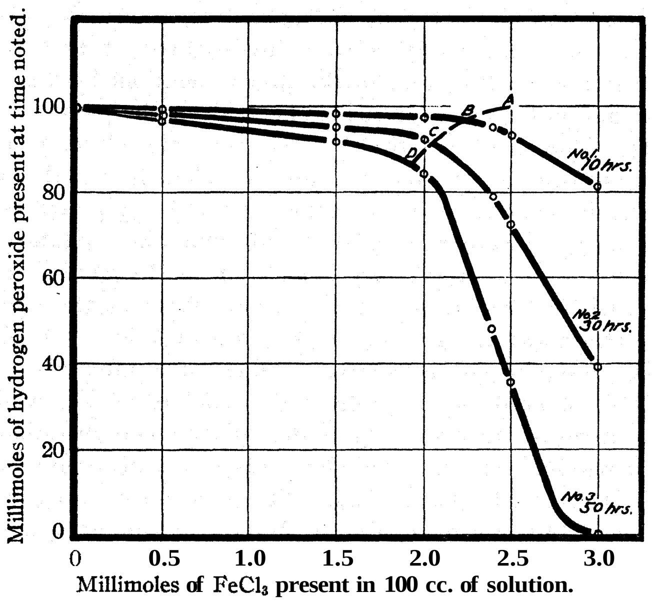
[1] This investigation was made possible by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

[2] Walton and Christensen, THIS JOURNAL, 48, 2083 (1926).

[3] Hatcher, Trans. *Roy. Soc. Canada*, 17, 319 (1923).

[4] Hatcher and Holden, *ibid.*, 18, 231 (1921).

catalyst. With this acid, the catalyst used was ferric chloride. It was impossible to study satisfactorily the reactions in the presence of the copper salts as catalysts due to the fact that a precipitate was formed. It was noted that with ferric chloride the oxidation efficiency[6] was low and that the hydrogen peroxide was completely decomposed before more than a small fraction of the oxalic acid had been oxidized. (This is shown in Fig. 1.) It was difficult to follow the changes in acidity when the temperature was above 25° due to the rapidity of the decomposition of the hydrogen peroxide, which increased with increase in temperature more rapidly than did the rate of oxidation of the oxalic acid.



Dotted curve, millimoles of oxalic acid present in 100 cc. of solution.

Fig. 1.—The oxidation of oxalic acid (graph indicating formation of complex).

The most interesting and perhaps the most important observation resulting from this work was the tendency of the oxalic acid to inhibit the decomposition of hydrogen peroxide by ferric chloride. A similar property of oxalic acid was observed by Colin and Senechal[6] in their study of the effect of acids on the catalytic oxidation of phenols by hydrogen peroxide in the presence of ferric salts as catalysts. These investigators

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[5] The term oxidation efficiency is applied to the ratio of the oxygen actually used to that available from the hydrogen peroxide. This function is used only qualitatively,

[6] Colin and Senechal, Compt. *rend.,* 153, 76-79, 282-283 (1911).

postulated the formation of a complex between the ferric ion and the oxalate ion. As further substantiation of the existence of this complex, they advance the fact that when an excess of oxalic acid is added to a solution containing a little ferric salt, neither potassium ferrocyanide nor potassium thiocyanate shows a test for iron. Their data do not indicate the possible composition of the complex. They indicate the formation of similar complexes of ferric ion with acetic acid, lactic acid, malic acid, tartaric acid and citric acid, in the order of increasing stability, the ferrioxalate complex being the most stable of all.

In the present study the rate of decomposition of hydrogen peroxide by ferric chloride in the presence of oxalic acid was found to be extremely slow when the molar concentration of ferric chloride was less than that of the oxalic acid. It increased rapidly, however, as the ferric chloride concentration increased beyond that of the oxalic acid. This indicated the formation of a definite and stable complex consisting of equimolecular quantities of ferric ion and oxalate ion.

This relationship is shown by the data in Table I and is illustrated graphically in Fig. 1, in which the concentration of the hydrogen peroxide in solutions containing various concentrations of ferric chloride is given at the time intervals, 10, 30 and 50 hours, respectively. In the three curves a change takes place in the reaction when the molar concentration of the ferric chloride exceeds that of the oxalic acid. For curve 1 the break occurs at the point at which the concentration of ferric chloride is 2.2 millimoles. In curves 2 and 3 it will be noticed that the break takes place at a concentration somewhat below this value. This is due to the fact that even in the lower concentrations of ferric chloride, oxidation of the oxalic acid is slowly taking place, so that after ten hours slightly less than 2.5 millimoles of the acid is present,

TABLE I

THE OXIDATION OF OXALIC ACID

Catalyst concn.	Start		After 10 hours		After 20 hours		After 30 hours		After 40 hours		After 50 hours	
$FeCl_3$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.
0.500	100.0	2.500	99.5	..	99.0	..	98.3	..	97.6	..	97.0	..
1.500	100.0	2.500	98.5	2.41	96.7	2.34	95.2	2.27	93.5	2.22	91.5	2.15
2.000	100.0	2.500	97.7	2.39	95.7	2.33	92.3	2.22	87.5	2.12	84.2	2.05
2.400	100.0	2.500	95.2	2.16	88.0	2.10	79.0	1.88	65.0	1.77	48.0	1.73
2.500	100.0	2.500	93.7	2.22	84.6	2.10	72.2	1.99	57.0	1.88	36.0	1.67
3.000	100.0	2.500	81.2	2.36	59.5	2.27	39.0	2.16	19.0	2.10	0.0	2.05

The dotted curve A-D represents this variation of acid concentration, expressed in the units denoted in the abscissa legend, paint "A" representing the concentration of oxalic acid (2.5 millimoles) corresponding to a ferric chloride concentration of 2.5 millimoles, at the beginning of the run. Point "B" is the catalyst concentration at which the oxalic acid concentration is reduced to its equivalent (2.2 millimoles) in ten hours. Point "C" is the catalyst concentration at which the oxalic acid is reduced in concentration to its equivalent in thirty hours, and point "D" the catalyst concentration at which the oxalic acid is reduced to its concentration in fifty hours. In other words, curve A-D is a line passing through those points on the isotemporal curves at which the oxalic acid concentration equals, molecularly, the ferric chloride concentration. These values were obtained by interpolation of the accompanying oxalic acid data.

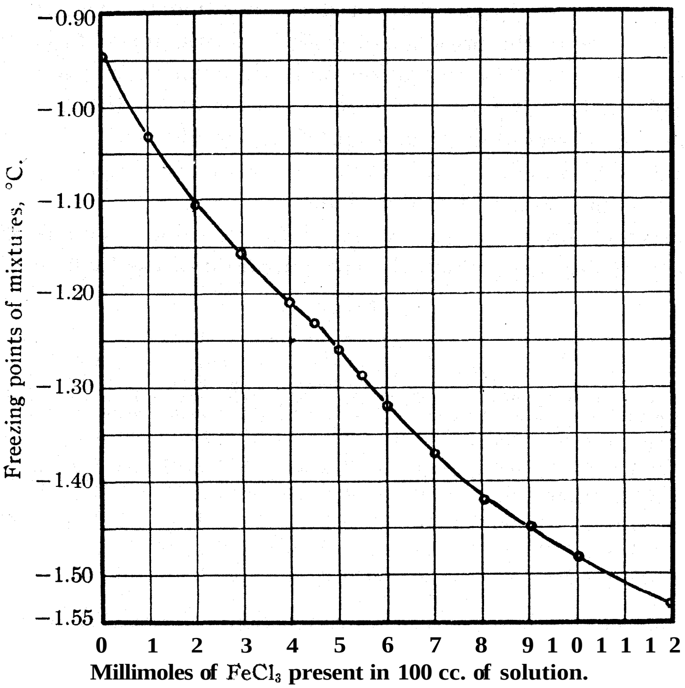

Fig 2.—Freezing point-composition curve for solutions containing 50 cc of 3% H_2O_2, 5 mmls. of oxalic acid, and varying quantities of $FeCl_3$ as noted.

Since runs made at temperatures of 25, 35 and 45° show the same relationship, the temperature of the reaction does not in any way alter the nature of the complex formed. Runs made with concentration of oxalic acid from 0.1 *N* to 0.05 N both showed the equimolecular relationship.

In order to determine the effect of the hydrogen ion, a run was made in which sodium oxalate was substituted for oxalic acid. This run gave results in exact accordance with those of the oxalic acid. The speed of reaction was greater, however, due to the fact that the presence of free acid suppresses the formation of ferric *acid*,[2,7] the intermediate both in the decomposition of the hydrogen peroxide and in the oxidation reactions.

The conclusion that a definite, stable complex was formed is further substantiated by freezing point measurements which, for varying quantities of ferric chloride in the presence of constant concentrations of oxalic acid and hydrogen peroxide, showed a slight break in the freezing point–composition curve, at the point where the molecular concentration of the oxalic acid equaled that of the ferric chloride. This freezing point–composition curve is given in Fig. 2, which represents concentrations of ferric chloride varying from zero to 12 millimoles per 100 cc.

The data for this curve are given in Table II.

Freezing point measurements with ferric chloride and oxalic acid in the absence of hydrogen peroxide showed no break in the freezing point curve; consequently the complex formed is not a simple compound of ferric chloride and oxalic acid.

TABLE II

FREEZING POINT–COMPOSITION DATA FOR SOLUTIONS CONTAINING 50 CC. OF 3% HYDROGEN PEROXIDE, 5 MILLIMOLES OF OXALIC ACID AND VARYING QUANTITIES OF FERRIC CHLORIDE, PER 100 CC. OF SOLUTION

$FeCl_3$ present in 100 cc. soln., mmls.	Freezing point	$FeCl_3$ present in 100 cc. soln., mmls.	Freezing point
0	−0.944	5.50	−1.287
1.00	−1.030	6.00	−1.320
2.00	−1.107	7.00	−1.372
3.00	−1.157	8.00	−1.422
4.00	−1.212	9.00	−1.447
4.50	−1.232	10.00	−1.482
5.00	−1.262	12.00	−1.532

Formic Acid.—Since formic acid is one of the intermediates formed in the oxidation of some of the more complex acids a study of its oxidation was undertaken. The data obtained were of value only in that they showed that formic acid was much more readily attacked by hydrogen peroxide in the presence of ferric chloride than in the presence of copper salts, and that the presence of carbon dioxide in the solution played an important role in determining the rate of the oxidation, markedly decreasing the rate when ferric chloride was used as the catalyst. The end products were carbon dioxide and water.

Other Oxidations.—Other reactions studied were the oxidation of succinic acid and its α-hydroxy derivatives, malic, tartaric and lactic acids. It was observed that the introduction of the hydroxy groups made the acids more readily oxidizable and, except for the case in which ferric chloride was used as the catalyst, decreased the ability of the acid

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[7] Bohnson and Robertson, THIS JOURNAL, 45, 2493 (1923).

to inhibit the decomposition of the hydrogen peroxide. It was further noted in the case of malic and lactic acids, both of which contain the structure —$CH_2CHOHCOOH$, that the concentration of the catalyst within the limits studied (0.005 M to 0.02 M) had very little effect either on the oxidation itself or on the rate of decomposition of the hydrogen peroxide.

The oxidations of glycerine and of ethylene glycol were also studied. In the case of these polyhydric alcohols, the acidity, due to formic acid as an intermediate, increased to a maximum. After the alcohol was almost gone, the acidity began to fall rapidly. In an earlier part of this paper attention was called to the fact that formic acid alone is readily oxidized. As a consequence one could expect that any formic acid formed as an intermediate would rapidly disappear. As such is not the case, it must be concluded that the presence of a hydroxyl group attached to a primary carbon atom exerts a protective action over formic acid in the presence of hydrogen peroxide and any of the catalysts studied. That is,

TABLE III

THE OXIDATION OF VARIOUS ORGANIC COMPOUNDS BY HYDROGEN PEROXIDE IN THE PRESENCE OF CERTAIN CATALYSTS AT A TEMPERATURE OF 25°

Catalyst used	Compound studied	Time in hours			Ref. numbers for variation of acidity (see notes below)
		For $^1/_2$ decomp. of H_2O_2	For $^1/_2$ oxidation of acid	For acidity to reach maximum	
1.00 mml. $FeCl_3$	Succinic acid	7	..	...	1
	Malic acid	22	43	...	2
	Lactic acid	8	..	10	3
	Tartaric acid	20	12	...	2
	Ethylene glycol	4	..	3	3
	Glycerine	$2^1/_2$	..	10	3
1.00 mml. $CuCl_2$	Malic acid	120	..	...	1
	Lactic acid	700	..	...	4
	Tartaric acid	220	..	80	3
	Tartaric acid (reduced pressure)	$1^1/_2$	3	...	2
	Ethylene glycol	500	..	550	3
	Glycerine	420	..	600	3
1.00 mml. $CuSO_4$	Succinic acid	350	..	180	3
	Malic acid	80	1000	...	2
	Lactic acid	200	..	150	3
	Tartaric acid	4	10	.	2
	Tartaric acid (reduced pressure)	12	..	4	3
	Ethylene glycol	300	..	300	3
	Glycerine	170	..	250	3

Notes: (1) falls very slowly with the loss of less than 50% of the acid during the life of the hydrogen peroxide; (2) falls smoothly and regularly; (3) rises to maximum and then falls smoothly; (4) shows initial sudden drop followed by gradual rise until hydrogen peroxide is exhausted.

the rate of oxidation of formic acid is much slower than in the absence of the alcohol. This protective action is apparently strictly a property of the primary carbinol, as no such marked effect was noted in the cases of tartaric and malic acids.

A general summary of these reactions is given in Table III. It is evident that, aside from the brief generalizations just outlined, it is impossible to express the relative oxidizability of these compounds quantitatively. This is due to the general complexity of the system, in which different parts of the molecule are undergoing simultaneous oxidation at different rates, accompanied in most cases by,the formation of a number of oxidation intermediates. At the same time the catalytic decomposition of the hydrogen peroxide is also going on. A number of varying factors, moreover, all have marked effects on the reaction. The increase in hydrogen ion concentration tends in all cases to inhibit both the decomposition of the hydrogen peroxide and any simultaneous reaction of oxidation. The carbon dioxide content, on the other hand, while having a marked effect, is less regular. When the carbon dioxide was removed by suction during the oxidation of tartaric acid, it was found that when copper sulfate was used as the catalyst the rate was decreased to one-third of the original value, while in the case of copper chloride it was increased over 100 times. It is the number of such variable factors, impossible to control completely and most difficult to interpret accurately, that makes it almost impossible to reach a quantitative expression for the relationships between structure and facility of oxidation.

Summary

1. Oxalic acid combines with the ferric ion in the presence of hydrogen peroxide to form a stable complex in which there is one mole of ferric ion for each mole of oxalate.

2. The introduction of hydroxy groups into the succinic acid molecule, giving malic and tartaric acids, increases the rate of its oxidation by hydrogen peroxide in the presence of catalysts and tends in general to decrease its ability to inhibit the decomposition of the hydrogen peroxide by the catalysts studied.

3. The carbon dioxide content of the reacting solution has a marked effect on the nature of the reaction.

4. An increase in acidity tends to decrease both the rate of decomposition of the peroxide and the rate of oxidation of the acid.

5. In the presence of the lactic acid structure, $—CH_2CHOHCOOH$, when copper salts are used to catalyze oxidation with hydrogen peroxide, the concentration of the catalyst, within the limits studied, has little effect either on the oxidation itself or on the rate of decomposition of the hydrogen peroxide.

6. The presence of a primary alcohol group exerts a protective action over formic acid in the presence of hydrogen peroxide and any of the catalysts studied, making the rate of oxidation of such an acid as formic or acetic, much slower than in the absence of the alcohol.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE PREPARATION OF BORIC ACID ANHYDRIDE AND ITS EFFICIENCY AS A DRYING AGENT

BY JAMES H. WALTON AND CHESTER K. ROSENBAUM

RECEIVED MARCH 27, 1928 PUBLISHED JUNE 5, 1928

Boric acid anhydride has been used by Schlesinger in the preparation of pure, dry formic acid[1] and also in the preparation of dry ether.[2] Since this substance is so efficient as a drying agent, it was of interest to determine the conditions which yield a product of maximum drying efficiency.

Preparation of Boric Acid Anhydride.—Fifty grams of pure boric acid crystals were placed in a 100-cc. platinum dish and heated over a Méker burner to a temperature of about 600°, a process attended by considerable frothing and the evolution of water vapor. The dish containing the clear, viscous liquid was then placed in an electrically heated muffle furnace and different samples were dehydrated at various temperatures for about an hour. At the end of this time, the dish was removed and the contents poured on a marble slab, where it immediately hardened to a clear glass. Although the boric acid melts at 577° a temperature of 800° is necessary for sufficient fluidity to permit easy pouring. Samples of the anhydride were dehydrated at 800, 900 and 1000".

The glassy boric anhydride is extremely hard and is best ground in a ball mill using flint pebbles. After grinding for three days a powder was obtained that passed through a 100-mesh sieve, 90% of it passing through a 160-mesh sieve. To help eliminate this prolonged grinding a sample of the anhydride was prepared at 900° and the molten glass poured into purified carbon tetrachloride that had been chilled to 0°. This yielded material in the shape of small pellets which could be much more easily ground after evaporation of the carbon tetrachloride. Some of this preparation was used in the following tests.

In view of the fact that it has been stated that boric acid anhydride vaporizes at a red heat,[3,4] it should be possible to take advantage of this property for the preparation of this substance in a finely divided form and thus avoid the use of the ball mill. Preliminary experiments with this method were unsatisfactory. To effect volatilization in a current of dry air, a temperature of 1000° was necessary. The experiments were not continued because of the small yield and the fact to be shown later that boric acid prepared at high temperatures is not a satisfactory drying agent.

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[1] Schlesinger and Martin, THIS JOURNAL, 36, 1589 (1914).

[2] Communication from Professor Schlesinger.

[3] Ebelmen, *Ann. chim.* phys., 22, 211 (1848).

[4] Tiede and Birnbrauer, Z. *anorg. Chem.*, 87, 129 (1914).

Analysis of Ground Boric Oxide.—Since pulverizing in the ball mill introduced a certain amount of mineral matter, the boric acid was tested for purity by titration with alkali in the presence of glycerine.

The sample to be analyzed was first heated to practically constant weight at 600°. The amount of water given off under these conditions varied from 3.2 to 3.5% and is largely uncombined water. The anhydride present in the various samples was as follows.

Temperature at which sample was prepared	800°	900°	1000°	900° (Chilled in CCl_4)
Boric oxide, %	76.1	74.4	62.3	58.6

The Drying Efficiency of Boric Acid.—This was determined by passing air saturated with moisture through tubes of the anhydride. The apparatus used was similar to that described by Willard and Smith.[5] This permitted air to be passed through a flowmeter and saturated with moisture, after which it passed through a U-tube which contained the boric oxide. The tube was 18 cm. high with an inside diameter of 7 mm. It contained about 3 g. of boric oxide supported by cotton wool to prevent packing. The column of boric oxide was 7 mm. in diameter and 20 cm. long. This U-tube was followed by a weighed phosphorus pentoxide U-tube, the function of which was to show the amount of moisture that escaped absorption by the boric oxide.

Absorption Capacity.—Upon passing moist air over the boric oxide at a rate of 2 liters per hour, it was found that the boric oxide was efficient until moisture to the extent of about 28% of its weight had been absorbed. The change from the anhydride to the metaboric acid requires 25.8% of water. This reaction takes place rapidly,[6] while the change from meta to the ortho acid is comparatively slow, which indicates that the absorption of water vapor is attended primarily by the formation of the meta acid.

Induction Period.—Freshly ground boric oxide shows a reluctance to combine with moisture until a certain volume of the moist gas has been passed through the absorption tube. The following data show, moreover, that this volume is greater for the samples of boric acid prepared at higher temperatures.

Air saturated with water vapor at 23° was passed at a rate of 2 liters per hour over boric oxide which had been prepared at 800°. For the first two liters of air 0.0012 g. of moisture was unabsorbed; for 6 liters more the total unabsorbed moisture was 0.0018 g. With boric oxide prepared at 900° efficient absorption began only after 13 liters of air had been passed through the absorption tube, while with the 1000° preparation 21 liters was necessary. The boric oxide prepared by chilling the 900° preparation to 0° by pouring the melt into carbon tetrachloride required

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[5] Willard and Smith, THIS JOURNAL, **44**, 2255 (1922).

[6] Meyers, *J. Chem. Soc.*, **111**, 172 (1917).

a passage of only 4 liters of dry air before it began to dry efficiently. Meyers[6] believes that when boric oxide is prepared at a temperature above 800°, molecular complexes are formed whose rate of reaction with water is much slower than the reaction of the boric oxide prepared at lower temperatures. The existence of such complexes would explain the "period of induction."

While an absolute comparison of the drying efficiency of the boric acid anhydride is difficult to make, these experiments indicate that this material is more efficient than sulfuric acid and calcium chloride but is somewhat inferior to phosphorus pentoxide and magnesium perchlorate.

With a drying column 40 cm. long and 7 mm. in diameter the boric oxide absorbed all the moisture from 88 liters of air saturated with moisture at 23° and flowing at the rate of 2 liters per hour.

Summary

1. In preparing boric oxide for drying purposes the boric acid should be dehydrated at about 800°. If prepared above this temperature, the product shows an induction period which decreases its efficiency.

2. The formation of a hard glass on cooling may be partly avoided by pouring the fused boric oxide into carbon tetrachloride at 0°. The resulting fragments are fairly easy to powder and the product is a very satisfactory drying agent.

3. The boric oxide was found to be an efficient drying agent until its moisture content rose to about 25% of its own weight.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF NEW YORK UNIVERSITY]

THE SYSTEM LITHIUM PERCHLORATE-WATER

BY JOHN P. SIMMONS AND CLARENCE D. L. ROPP[1]

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According to A. Potilitzin,[2] aqueous solutions of lithium perchlorate give the trihydrate, $LiClO_4 \cdot 3H_2O$, which loses approximately two-thirds of its combined water when heated between 98 and 100°, changing to monohydrate, and all of its water between 130 and 150°. The approximate nature of these data makes apparent the need of a more careful study of this system.

Preparation of Lithium Perchlorate

Anhydrous lithium perchlorate was made by the method of Richards and Willard.[3] The purity of the salt was proved by a modification of a

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[1] The results of this investigation were submitted by Clarence D. L. Ropp as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Potilitzin, J. *Russ. Phys.-Chem. Soc.*, 19, 339 (1887); 20, 541 (1888).

[3] Richards and Willard, THIS JOURNAL, 32, 4 (1910).

method by Lamb[4] for the analysis of perchlorates. This consists in heating a weighed amount of lithium perchlorate in a Pyrex test-tube loosely plugged with asbestos. The loss in weight is assumed to be due to the oxygen driven off. As an illustration, two such determinations gave 100.10 and 100.15% of lithium perchlorate.

Procedure

In order to establish accurately the number and composition of the hydrates of lithium perchlorate capable of existing between 0° and the temperature where the anhydrous salt is stable, the following experiments were made.

(1) Saturated solutions of lithium perchlorate were cooled from temperatures between 0 and 90°, approximately. As a result, long, needle shaped crystals formed which, after careful drying between filter paper, showed upon analysis a water content of 33.90%, which agrees well with the corresponding theoretical value for the trihydrate, 33.68%.

(2) A quantity of this trihydrate was powdered and placed in a desiccator over anhydrous lithium perchlorate and kept thus for a period of six weeks. This experimental arrangement causes the trihydrate to change to the next lower hydrate. Determinations of the water content of the specimen were made at frequent intervals and the percentage of water finally became constant at 14.52%. The theoretical value for $LiClO_4 \cdot H_2O$ is 14.48%.

(3) A synthetic lithium perchlorate monohydrate was made and this was used as a desiccating agent for crystals obtained by cooling solutions saturated between 0 and 90° and which by experiment[2] were proved to be $LiClO_4 \cdot 3H_2O$. The latter showed constancy in water content at 33.66%, which agrees with the corresponding value for $LiClO_4 \cdot 3H_2O$, 33.68%.

The results of these three sets of experiments indicate that lithium perchlorate forms two hydrates, $LiClO_4 \cdot 3H_2O$ and $LiClO_4 \cdot H_2O$ and that evidence of the existence of a dihydrate does not exist. The system was not investigated below 0°.

To obtain more precise information regarding the transition points involved in this system, solubility measurements were made over a temperature range from 0 to 170°. These measurements were made at the lower temperatures by agitating an excess of anhydrous salt with water in a solubility tube kept at constant temperature in a thermostat until constancy in concentration was reached. These determinations were supplemented by results obtained by sealing in a tube known quantities of anhydrous lithium perchlorate and water, immersing the tube in water and gradually heating until the solid phase disappeared. The tube was

[4] Lamb and Marden, THIS JOURNAL, 34, 812 (1912).

then cooled until the hydrate, stable at the temperature being used, crystallized out. The tube was then heated carefully one-tenth of a degree at a time with constant agitation and the temperature noted at which the last trace of solid phase disappeared. The solubility measurements at the higher temperatures were all made by the second method. Solubility data for the temperatures indicated are given in Table I.

TABLE I

SOLUBILITY OF $LiClO_4$ IN GRAYS PER 100 OF SOLUTION

Temp, °C.	Concn.	Temp., °C.	Concn.	Temp., °C.	Concn
0[a]	29 90	92.3	62 5	108 9	72 8
10	32.88	94.3	65 0	120 7	75 0
20	35.95	95 1	66 32	136 9	80 0
25	37.48	94 8	66 67	144 0	82 5
30	38 87	93 2	70 0	148 5	85 0
40	41.97	92 7	70 3	149 3	87 5
64 6	50.0	92 53	70 33	144 3	90 0
77.9	55.0	93.2[b]	7 0 5	167.5[c]	9104
89 2	60 0	97 3	71 0	172	91 11

[a] Trihydrate is solid phase.
[b] Monohydrate is solid phase.
[c] Anhydrous salt is solid phase.

Density values of the saturated solutions at the lower temperatures were made by weighing a known volume and are given in Table II.

TABLE II

DENSITIES OF SATURATED SOLUTIONS OF $LiClO_4$

0°	10°	20°	25°	30°	40°
1.215	1.236	1.258	1.269	1.277	1.300

H. H. Willard and G. F. Smith[5] determined the solubility of lithium perchlorate in water at 25°, obtaining a value of **37.385%** and a density of 1.268, which agree very well with our values of 37.48% and a density of **1.269.**

The melting point of anhydrous lithium perchlorate was determined by Potilitzin[2] and by Richards and Willard[3] as 236°, and this value was used in the construction of the solubility curve in Fig. **1.** An inspection of the solubility curve of lithium perchlorate, Fig. 1, indicates clearly two transition temperatures and two congruent melting points. The melting point of $LiClO_4 \cdot 3H_2O$ from the curve is 95.1°, which agrees well with Potilitzin's[2] value of 95°. The melting point of $LiClO_4 \cdot H_2O$ from the curve is 149° for a content of 86.5% of $LiClO_4$. The theoretical value is 85.52%.

In order to determine the transition points with greater accuracy than could be attained by use of the solubility data, cooling experiments were

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[5] Willard and Smith, THIS JOURNAL, 45, 286 (1923).

performed. Marked halts in temperature drop were observed at 92.53 and 145.75°. These temperature points indicate the transition points for $LiClO_4 \cdot 3H_2O \rightleftarrows LiClO_4 \cdot H_2O$ and $LiClO_4 \cdot H_2O \rightleftarrows LiClO_4$, respectively.

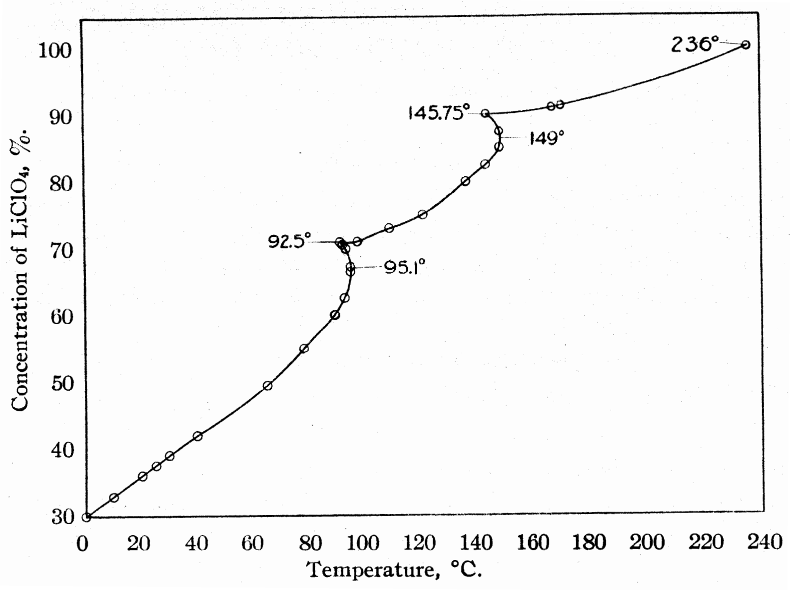

Fig. 1.

Summary

1. Solubility measurements of $LiClO_4$ in water over a temperature range from 0 to 170° have been made.
2. Density values of the saturated solutions over a temperature range from 0 to 40° have been made.
3. The existence of $LiClO_4 \cdot 3H_2O$ and $LiClO_4 \cdot H_2O$ is definitely established.
4. No evidence of the existence of a dihydrate was observed.
5. The transition point $LiClO_4 \cdot 3H_2O \rightleftarrows LiClO_4 \cdot H_2O$ is 92.53°.
6. The transition point $LiClO_4 \cdot H_2O \rightleftarrows LiClO_4$ is 145.75°.
7. The melting point of $LiClO_4 \cdot 3H_2O$ is confirmed at 95.1°.
8. The melting point of $LiClO_4 \cdot H_2O$ is 149°.

NEW YORK CITY

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

THE RATE OF OXIDATION OF HYDROGEN PEROXIDE BY BROMINE AND ITS RELATION TO THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN A BROMINE-BROMIDE SOLUTION

BY WILLIAM C. BRAY AND ROBERT S. LIVINGSTON

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Introduction

The catalytic decomposition of hydrogen peroxide in a hydrobromic acid solution has been shown to be due to the simultaneous oxidation and reduction of hydrogen peroxide by bromine and by bromide ion, respectively.[1] The rate of decomposition, at constant ionic strength, is given by the following equation

$$-\mathrm{d}(\mathrm{H_2O_2})/\mathrm{d}t = K(\mathrm{H_2O_2})(\mathrm{Br}^-)(\mathrm{H}^+) \qquad (1)$$

Similarly, the steady-state bromine concentration may be written as

$$(\mathrm{Br_2}) = R/(\mathrm{H}^+)^2(\mathrm{Br}^-)^2 \qquad (2)$$

The simplest kinetic mechanism consistent with these facts postulates the occurrence of two rate determining reactions, the formation and reduction of hypobromous acid

$$\mathrm{H_2O_2} + \mathrm{Br}^- + \mathrm{H}^+ = \mathrm{HBrO} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{H_2O_2} + \mathrm{HBrO} = \mathrm{H}^+ + \mathrm{Br}^- + \mathrm{O_2} \qquad (4)$$

and a rapid reversible equilibrium, the hydrolysis of bromine.

In agreement with this mechanism it was found[2] that the rate of oxidation of bromide ion by hydrogen peroxide (at a distance from the steady state) can be represented by an equation having the same form as the law of catalysis (Equation 1), but with a constant half as great, $K_1 = K/2$.

It seems probable, therefore, that the rate of reduction of bromine by hydrogen peroxide can be represented, in agreement with the mechanism, by the following equation

$$-\mathrm{d}(\mathrm{H_2O_2})/\mathrm{d}t = K_2(\mathrm{Br_2})(\mathrm{H_2O_2})/(\mathrm{Br}^-)(\mathrm{H}^+) \qquad (5)$$

where $K_2 = K/2R$. It is difficult to obtain an accurate measure of this rate. When the bromide and hydrogen ion concentrations are low enough to render the catalytic rate negligible, the rate of the reduction is so rapid at 25° that it practically cannot be measured by any ordinary method. Two measurements were made[3] in an intermediate range, where the rate is fast but measurable, and the catalytic rate is not negligible but can be corrected for by a method involving a series of approximations. Although the results of these two measurements are in agreement with the predic-

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

[2] (a) Ref. 1, pp. **1265–7,** Tables VII and VIII (5 experiments); (b) Livingston and Bray, THIS JOURNAL, 45, **2052** (1923), Table IV (1 experiment).

[3] Ref. 1, pp. **1268–9,** Tables IX and X.

tions based upon the mechanism, they do not constitute a satisfactory *independent* proof of the validity of Equation 5. The purpose of the present paper is to furnish such a proof.

The rate measurements of Balint[4] at 0°, which furnish strong evidence in favor of Equation 5 but were overlooked until after our work was completed, will be discussed later. The objections of Christiansen[5] to our conclusions will also be considered.

Methods

A method for measuring reaction velocities can only be applied when the half time of the reaction is large compared to the time required for mixing the component solutions. The time required for mixing moderately large volumes by simple hand shaking may be as great as one minute. By the use of very small volumes and special apparatus the time can be reduced to less than a second.[6]

Probably the simplest way of obtaining rapid mixing is by means of a flow method. Stewart and Edlund[7] used a flow method of mixing in their study of a bimolecular gas reaction. They estimate that with their apparatus mixing was complete in less than a second. Hartridge and Roughton[8] have made an extensive study of the application of flow methods to the determination of rapid reaction velocities in aqueous solutions. In their apparatus the mixing occurs in a small cylindrical, or conical, chamber into which tangential jets of the component solutions are forced. They followed the course of the reaction either by measuring the absorption spectra of the solution, or by determining the change in its temperature due to the heat of the reaction. They estimate[8b] that their perfected apparatus is capable of measuring the rate of a reaction having a half time as small as one thousandth of a second.

The apparatus described here was designed to measure the rates of reactions having half times of from one-half to six seconds. It is represented schematically in Fig. 1.

The three-liter **flasks, A** and **A'**, serve as reservoirs for the component solutions. C is the mixing chamber and D the reaction tube. E, E' and E'' are outlets, controlled by the large two-way stopcocks, P and P'. F is a second mixing chamber, which can be placed beneath either outlet E or E'. H is a Bunsen stirrer, driven by an 1800 r.p.m. motor. I is an overflow tube, leading to a collecting vessel; this tube can be converted into a siphon by closing stopcock O. **A** nitrogen cylinder was connected to tube J through a reducing valve. The nitrogen pressure was further controlled by the mercury

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[4] Balint, Thesis (in Hungarian), University of Budapest, **1910**.

[5] Christiansen, (a) *Z. physik.* Chem., **117**, 453 (1925); (b) ibid., **128**, 430 (1927).

[6] See C. Benedicks, ibid., **70**, 12 (1910).

[7] Stewart and Edlund, THIS JOURNAL, 45, 1014 (1923).

[8] Hartridge and Roughton, (a) Proc. Roy. *Soc.* (London), **104A**, 376 (1923); (b) Proc. *Camb.* Phil. *Soc.*, **22**, 426 (1924); (c) see also the recent work of Saal, Rec. *trav.* chim., **47**, **73** (1928).

regulator, K, and was measured by the open manometer, L The apparatus was constructed entirely of Pyrex glass

The mixing chamber, C (see detail C, Fig. 1), consists of a "Y" tube made from *flattened* capillary tubing. It is 4.5 cm. long, and has a volume of 0.12 cc. As is indicated in the figure, the flattened capillaries are so arranged that the surface of contact between the two component solutions is as large as possible. This type of mixing chamber, which was suggested by Professor Branch of this department, has the advantage of producing complete mixing at slow as well as at rapid rates of flow, and of having a very small volume. It has the disadvantage of offering a considerable resistance to the flow, and thereby limiting the range of reaction rates which can be measured.[9]

The reaction tube D was made of 0.70 cm. tubing. The volumes of the tube to the ends of E and E' are 18.04 and 30.9 cc., respectively. The large two-way stopcocks were bored to 0.70 cc. and did not produce a constriction in the tube.

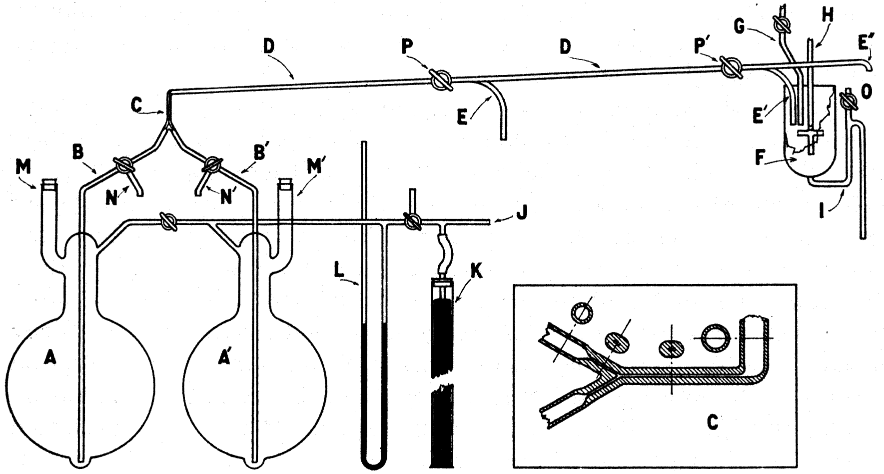

Fig. 1.—Apparatus.

Temperature control was obtained by submerging the reservoir flasks, A and A', in a thermostat and wrapping tubes B, B', C and D with asbestos and friction tape. This wrapping also protected the reacting mixture from light. To test the effectiveness of the temperature control, measurements were made of the temperature of the solution emerging at E or E', when the apparatus was operating under the conditions of an actual experiment. With room temperature about 20° and the temperature of the thermostat at 25.0° and at 35.2°, the temperature of the emergent solution was 25.0 and 34.8°, respectively.

In principle the flow method is identical with the customary methods of determining reaction velocities; it consists of the determination of the concentration of the reactants before and after a known interval of time. In the method presented here, this interval begins when the reactants are brought together in some element of volume, and ends when the reaction,

[9] For a discussion of the general problem of rapidly mixing solutions by flow methods and of following the progress of the reaction (by physical methods) in the resulting solution, see Hartridge and Roughton, ref. 8

occurring in that volume, is stopped by mixing with a third solution. We may take this as equal to the time, τ, required for an element of volume to pass from the mixing chamber, C, through the reaction tube, D, to the end of the outlet, E or E'. Therefore

$$\tau = Ut/V \tag{6}$$

where U is the volume of the reaction tube and V the volume of solution delivered in time t. The results of a series of calibrations, using pure water at 25°, can be represented with fair accuracy for pressures between 20 and **38** cm. of mercury by the following equation

$$\tau = U/(11.0P + 174) \tag{7}$$

τ is expressed in minutes, U in cc., and P (the pressure) in cm. of mercury. The value of τ is also slightly affected by the level of the solutions in the reservoir flasks; this correction never exceeds 3%, and for pressures above 30 cm. is negligible. τ is, of course, dependent on the viscosity of the solution; however, the rate of flow of the dilute solutions used in these experiments never differed from that of water by 1%. The flow was the same regardless of which outlet was used. The calibrations would have been useless if oxygen gas had been evolved in the reaction tube, but bubble formation was not observed in any experiment until after the mixture had emerged at outlet E or E'.

To determine the initial concentrations of the reactants it is necessary to know the concentrations of the stock solutions (in the reservoir flasks) and the relative amounts of these two solutions brought together in the mixing chamber C. Since the mixing chamber used was not exactly symmetrical, the volumes flowing from the two reservoirs were not equal. The relative amounts delivered were determined, under a variety of conditions, by introducing distilled water into one reservoir and 0.10 N tri-iodide solution into the other, and then analyzing the resultant mixture. A number of such experiments showed that, for pressures greater than 22 cm., 0.552 part of the total volume delivered came from flask A. For lower pressures, the value of this ratio increases gradually to 0.558, when the pressure is decreased to 18 cm. It is not affected by interchanging the water and tri-iodide solution. A small departure occurs when the levels of the two solutions in the reservoirs are not the same; thus a difference in level of 9 cm. caused the ratio to change by only 5%. The making of a correction was avoided by wasting (through outlet N or N′) the solution which was in excess until the levels were equal at the beginning of each experiment.

To determine the velocity of a rapid reaction by chemical means it is necessary not only to mix the component solutions rapidly but also, after a known short time, to stop the reaction by mixing the reacting solution with some appropriate solution. In general this third solution must contain some substance capable of reacting with (and thereby removing) one of the reaction components with extreme rapidity. In the experiments presented here we have utilized the reduction of bromine by iodide ion

$$Br_2 + 2I^- = 2Br^- + I_2 \qquad (8)$$

which Saal[8c] has recently shown to be completed in less than 0.004 sec. This reaction is followed by a comparatively slow one between hydrogen peroxide and iodide ion, since the solution used to stop the reaction always contained an excess of iodide, and sufficient acid to prevent the catalytic decomposition of the peroxide. The reacting mixture was delivered directly into a vessel, F, containing the iodide solution, which was stirred rapidly (see the description of Fig. 1). To maintain the iodide concentration, fresh iodide solution was added continuously and the mixture was allowed to overflow into a collecting vessel.

An iodimetric method of analysis was used in *determining hydrogen peroxide,* as well as bromine, the iodine liberated in acid solution being titrated with thiosulfate. The peroxide solution was pipetted into a solution which contained 2 g. of potassium iodide, 20 milli-equivalents of sulfuric acid and enough water to make the final volume 100 cc. The mixture, in a glass-stoppered vessel, was set aside in the dark for about forty minutes. After the titration with thiosulfate the mixture was again set aside for about twenty minutes; the absence of "after-bluing" was evidence that the reaction between H_2O_2, I^- and H^+ was complete under these conditions. It was found that no error was introduced by beginning the titration before the reaction was complete.[10] The low concentration of acid, 0.2 N, was used in order to minimize the oxygen error[11] due to reaction between O_2, I^- and H^+.

To check the accuracy of our method a solution of hydrogen peroxide was titrated with the potassium permanganate solution which had been used in standardizing the thiosulfate solution.[12] A small excess of potassium permanganate was added and this excess was determined iodimetrically. A 25.03cc. portion of the hydrogen peroxide solution was found to be equivalent to 20.90 and 20.92 cc. of thiosulfate by the potassium permanganate method, and to 20.93 and 20.93 cc. of thiosulfate by our iodimetric method.

In employing this method it is important that acid be present when the iodide and peroxide are mixed, since iodide alone catalyzes the decomposition of the peroxide into water and oxygen. Thus in two experiments in which the acid was added one minute and five minutes after the

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[10] Harcourt and Esson, J. *Chem. Soc.*, **20**, 476 (1867); Bell, J. *Phys. Chem.*, *7*, 61 (1903).

[11] This error seems unavoidable in the rapid method recommended by Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, **1924**, Vol. II, p. 576, since the acid concentration is 2.25 N.

[12] Bray and Miller, THIS JOURNAL, **46**, 2204 (1924).

peroxide and iodide were mixed, it was found that 12.5 and 45% of the peroxide had decomposed.[13]

The experimental procedure probably can be best explained by giving the details of an actual experiment (Table I, No. 8). The stock hydrogen peroxide solution was 0.04205 *M;* the stock bromine solution 0.02622 *M*. Both of them were 0.00063 M in respect to perchloric acid. One liter of acid–iodide solution was used; it contained 10 cc. of concentrated sulfuric acid and 25 g. of potassium iodide. The nitrogen pressure was 20.8 cm. The volume of the reaction tube was 30.9 cc. since outlet E′ was used. Immediately before the experiment about one liter of solution was wasted through E″. The experiment lasted 104 sec. (measured with a calibrated stop watch). The mixing chamber, F, overflowed into and was drained into a 2-liter graduated flask. About 245 cc. of water was required to make up the mixture (reaction mixture + acid–iodide solution) to two liters. The resulting solution contained 0.01908 oxidizing equivalent per liter. From these data and the calibrations we may compute the duration of the reaction and the concentrations of the reactants and products before and after this time interval.

At 20.8 cm. pressure, 0.554 part of the reaction mixture was made up from the hydrogen peroxide stock solution. Therefore

$$(H_2O_2)_0 = 0.554 \times 0.04361\ M = 0.02416\ M$$
$$(Br_2)_0 = B = 0.446 \times 0.02664\ M = 0.01188\ M$$
$$(H^+)_0 = C = 0.00063\ M$$

Referring to the calibrations again (see Equation 7), we find the reaction time, τ, is 0.00770 minute and the rate of flow is 6.70 cc./sec. With this flow 764 cc. should be delivered in 104 seconds. To obtain a check of this value we subtract the volume of the acid–iodide solution and the water used from two liters (2000 cc. − 1245 cc. = 755 cc.). This check was used to detect any gross error and in the experiments at 25° the volume calculated from the calibrations was used.[14] Knowing the volume of the

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[13] It is possible that this source of error may account for the low results of Wagner, Ind. *Eng. Chem.*, **17**, 973 (1925), in analyzing barium peroxide, since the order of mixing seems to have been peroxide, water, iodide, acid.

[14] The calculated and measured volumes differed by more than **1.2%** in only four experiments. Nos. **4, 7, 13** and **14.** The results based on the calculated volumes are shown in Table I, and those based on the measured volumes are given in the following table.'

Expt.	Diff. in vol., %	K_2, Table I	10' x	τ (min.)	K_2
4	4.3	0.0238	3.805	0.0807	0.0163
7	1.6	.0178	4.785	.0448	.0213
13	1.6	.0258	3.675	.0457	.0217
14	3.3	.0268	4.32	.0791	.0193

The new values of K_2 in the sixth column are in better agreement than the old ones with the values of K_2 in the remaining experiments (Table I).

In the two experiments at 35°, Nos. **20** and **21,** the calculations were based on the measured volumes.

solution delivered, as well as the concentration of oxidizing equivalents in the 2-liter sample, we may compute the sum of the concentrations of hydrogen peroxide and bromine in the solution delivered.

$$(H_2O_2) + (Br_2) = A + B - 2x = (2000/764)(0.01908/2) = 0.02500\ M$$

Combining this with the values of A and B we can obtain x, the loss in bromine (or peroxide) in moles per liter.

$$A + B = 0.02416 + 0.01188 = 0.03604\ M$$
$$x = {}^1/_2(0.03604 - 0.02500) = 0.00552\ M$$

To determine the rate constant from these data it is necessary to obtain the integrated form of Equation 5. Using the symbols already defined and letting $(Br^-)_0 = D$, we may write Equation 5 in the following form

$$dx/dt = K_2(A-x)(B-x)/(C+2x)(D+2x) \qquad (9)$$

By integrating and eliminating the constant we obtain

$$\tau K_2 = 4x + \frac{(2B+C)(2B+D)}{(A-B)} \ln \frac{B}{(B-x)} - \frac{(2A+C)(2A+D)}{(A-B)} \ln \frac{A}{(A-x)} \qquad (10)$$

It should be noted that in the derivation of this formula no allowance was made for the formation of tribromide, from bromine and bromide ion; however, this effect is negligible in the experiments presented here.[15]

Results and Conclusions

The experimental data are summarized in Table I. Three recent experiments, Nos. 15–17, made with our apparatus by H. A. Bois and B. Makower, are included; also the first point in each of our earlier experiments, Nos. 18 and 19. The second to fifth columns give the initial concentrations of hydrogen peroxide, bromine, acid and bromide, respectively. The acid added was perchloric, except in Expts. 18 and 19; the bromide in Expts. 16–19 was potassium bromide.

The values of K_2 given in the eighth column of Table I do not show any marked trend with the initial concentrations of. hydrogen peroxide, bromine or acid, nor with the duration of the reaction: we may conclude, therefore, that Equation 5 correctly represents the rate of the reaction. It is interesting to compare the values of K_2 in Expts. 18 and 19 (0.037 and 0.030) with the published values[3] (0.035 and 0.030), which were computed by a method involving successive approximations, and were based upon a series of analyses extending over an hour. The computing method then used allowed corrections to be made for the catalytic rate and for the formation of tribromide ion.

The values of K_2, however, do show a small trend, namely, an increase with the ionic strength, Col. 9. This is not surprising when it is remem-

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[15] The effect of tribromide is largest when the bromide concentration is small, and therefore would have been most serious in Expts. 3 and 12. In these cases it was estimated, by a method of approximations, that a correction for tribromide would have decreased the values of K_2 by not more than 10%.

Table I

Experimental Data and Calculations

Temp., 25°, in Expts. 1–19, 35° in Expts. 20 and 21

Expt. no	Initial concn , (moles per liter) X 10^3 H_2O_2	Br_2	H^+	Br	10^3x	τ, min.	K_2	μ, ionic strength	γ^2, (HBr)	$\chi_I = K_2\gamma^2$
1_A	22 66	11 63	0 28	0	4 865	0 0630	0 0171	0 00.52	0.90	0.0154
2.4	22 74	11 57	28	0	A 405	0773	0205	0057	.89	.0183
3_B	7 61	15 78	35	0	3 455	.0447	,0205	0038	.91	.0187
4_B[a]	7 61	I5 78	.35	0	4 145	0772	0238	0045	.91	.0216
5_B	761	15.78	.35	0	4080	.0778	0223	.0044	.91	.0202
6_C	24 16	11 88	63	0	4 685	0453	0196	.0053	.90	.0176
7_C	24 16	11 88	63	0	4 575	0456	0178	0052	.90	.0160
8_C	24 16	11 88	63	0	5 52	0770	.0208	0062	.89	.0185
9,	19 69	17 10	.03	0	5 14	0435	.0210	.0057	.89	.0187
10,	19 09	17.10	63	0	6 01	0752	0214	.0066	.88	.0189
11,	19 69	17 10	63	0	6 03	0759	.0217	.0067	.88	.0192
12_E	2386	1386	126	0	331	,0309	0242	0159	.82	.0198
13_E	23 90	13 83	12 6	0	3 92	0450	0258	,0165	.82	.0210
14_E[a]	23.90	13 83	12 6	0	4 795	.0765	0268	.0174	.81	.0217
15_F	1885	1115	060	0	4566	.0609	0195	.0052	.90	0176
16_G	20 12	11 88	20	2 25	4 497	.0605	0200	.0070	.88	.0176
17_G	20 12	11 88	20	2 25	3 819	0351	0203	.0063	.89	.0180
18_H[b]	152 0	57 2	380	9 55	36 8	5 0	0372	60	.34	.0127
19_K[b]	113 7	74 0	585	9 80	36 0	8 0	0297	.91	.33	,0098
20_L	18 89	9 89	0 63	*0*	5 31	0 0543	.0473	.0059	(.89)	(.0420)
21_L	1889	989	063	0	4645	.0315	0484	.0053	(.90)	(.0430)

[a] Rejected, see ref. 14.

[b] Ref. **3**.

bered that no allowance is made for the activities in Equation 5.[16] If we assume that the activity coefficients of the neutral molecules involved are equal to unity, we may write Equation 5 as follows

$$-d(H_2O_2)/dt = \chi_2(H_2O_2)(Br_2)/(H^+)(Br^-)\gamma^2_{HBr} \qquad (11)$$

where χ_2 is a true constant equal to $K_2\gamma^2_{HBr}$. This equation may be derived either by assuming that the rate is proportional to the activities of the components (in this case practically identical with the concentrations) or by assuming the correctness of Brönsted's[17] reaction velocity hypothesis. In all of the experiments except numbers 18 and 19, the ionic strength changed considerably during the reaction. Because of this it is impossible to determine accurately the value of χ_2. An approximate set of values can be obtained by assuming that for each experiment the ionic strength is constant and has a value equal to that for the solution when χ has a value half as great as its final value. Using the activity coefficients

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[16] See (a) Bronsted, Z. *physik. Chem.*, **102**, 169 (1922); (b) Livingston, This Journal, **48**, 53 (1926).

[17] (a) Bronsted, ref. 16 a; (b) *Z. physik Chem.*, **115**, 337 (1925); (c) Bronsted and Livingston, This Journal, **49**, 435 (1927); (d) Bronsted, "The Theory of Velocity of Ionic Reactions," Columbia University Press, **1927**.

of hydrobromic acid corresponding to these ionic strengths,[18] a series of values of χ_2, Col. 9, has been computed. The average value is 0.018. The results of Expts. 18 and 19 are not included in the average, but do not differ greatly from it. The discrepancy may possibly be due to experimental inaccuracies, but is more probably evidence that Equation 11 does not hold exactly at high ionic strength.[19] Otherwise, the variations in χ_2 are no greater than the experimental error.

We may combine the value of χ_2 with the average value of χ_1, 0.043/2,[19a] to obtain a value for the steady-state function, p.

$$p = \chi_1/\chi_2 = 0.043/2 \div 0.018 = 1.2 \qquad (12)$$

This value lies well within the range of values (0.9 to 2.6)[20] calculated from steady-state concentration measurements by means of the equation

$$p = R/\gamma^4 \qquad (13)$$

but is somewhat smaller than the mean value, 1.7, previously chosen. However, it seems probable that too great weight was then given to the larger values of p, which were based upon measurements made in the presence of sulfates and at high ionic strengths.

Balint's Results.—Equations 5 and 9 and the hypobromous acid mechanism were also obtained (in 1910) by Balint,[4] who measured the rate of reduction of bromine by hydrogen peroxide in aqueous solution at 0°. He followed the course of the reaction by measuring the change in volume or pressure due to the oxygen gas evolved, from 5 to 10 readings being taken during each run. His experiments appear to have been extremely well planned and accurate. He proved that the reaction corresponds quantitatively with the equation

$$H_2O_2 + Br_2 = O_2 + 2H^+ + 2Br^- \qquad (14)$$

but the stoichiometry was studied only in the absence of added hydrobromic acid, and he was apparently unaware of the reaction which occurs between H_2O_2, Br^- and H^+. Fortunately, we have been able to calculate, by means of an estimated value of K_1 at 0°, that the error introduced by this reaction is negligible in all his experiments, with the possible exception of No. 23. The initial concentrations and the results are summarized in Table II.

Balint calculated K_2 in Expts. 6–15 by a formula equivalent to Equation 10, and in Expts. 16–23 by assuming that the concentration of all substances except hydrogen peroxide remained constant during the reaction. All of the results were corrected (approximately) for tribromide formation, and in the second group of experiments a further correction was applied for the apparent degree of ionization of the electrolytes present. Since we

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[18] Livingston, THIS JOURNAL, 48, 45 (1926).

[19] Cf. (a) Livingston, *ibid.*, 48, 56 (1926); also (b) Livingston and Bray, *ibid.*, 47, 2076 (1925).

[20] *See* Table III, ref. 19a, p. 57.

TABLE 11

BALINT'S EXPERIMENTS AT 0°

	Nos. 6 to 15	Nos. 16 to 23	Final
Init. concn. (molal), H_2O_2	**0.00023-0.0049**	0.0011-0.0068	
Init. concn. (molal), Br_2	.00014- .0079	.043- .079	
Init. concn. (molal), H^+ (total acid)	.00075- .0426	.072- .534	
Init. concn. (molal), Br^- (total bromide)	.00219- .0120	.058- .623	
K_2, Balint, average	.000749	.000741	**0.000745**
K_2, without Balint's correction for ionization	.000749 ± 2.7%	.000936 ± 12%	
$\chi_2 = K_2\gamma^2$	.000635 ± 9%	.000605 ± 11%	.00062

believe that this latter correction is scarcely an admissible one, we have recalculated K_2 in these experiments (Nos. 16–23) using the stoichiometric concentrations. We have also applied the activity correction by the method already discussed (see Equation 11), with the assumption that the activity coefficient of hydrobromic acid has the same values at 0° as at 25°; the resulting values of χ_2 are shown in the last line of Table II, the final average being 0.00062.

Comparison of this value of χ_2 at 0° with our values at *25* and 35°, 0.018 and 0.043, leads to the conclusion that the temperature coefficient of the reaction (Equation 14) decreases with increasing temperature. This result and the temperature coefficient of the bimolecular reaction between hydrogen peroxide and hypobromous acid (Equation 4) will be discussed in another paper.

The Hypobromite Ion Mechanism Suggested by Christiansen.—From certain theoretical considerations, Christiansen[5] has concluded that hypobromite ion rather than hypobromous acid is involved in the reduction of bromine by hydrogen peroxide. An error in logic in his first theoretical treatment[5a] is corrected[21] in his recent paper.[5b] His general treatment covers the various possible special cases and includes those we have considered. Thus the conclusion that hydrogen peroxide reacts more rapidly with hypobromous acid than with hypobromite ion may be shown to follow from his general equation if the steady-state function is assumed to have the form shown in Equation 2. Christiansen, by basing his decision entirely on those measurements of the steady-state concentrations which were made with sulfuric acid at high concentration,[22] concludes that the steady-state function contains the concentration of hydrogen ion to the inverse third power and that, therefore, the reduction of bromine involves hypobromite ion rather than hypobromous acid. The experimental result that he cites is true only for concentrations of sulfuric acid greater than 1 *N* and we believe that it is not possible to draw from this

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[21] Cf. ref. 5 b, p. 434, lines 17–22.

[22] See Fig. 1, ref. 5 a, p. 434; and contrast the general agreement in Table III ref. 14 a, p. 57.

result any conclusion in regard to the mechanism of the simple reaction. It seems probable that this effect is due to the occurrence of side reactions, such as the formation of bromate ion.[23] However, since the question has been raised, it seems worth while to test the hypobromite mechanism with the data presented in this paper.

If we replace Equation 4 by the following expression

$$H_2O_2 + BrO^- = Br^- + O_2 + H_2O \tag{15}$$

and assume, as before, that the bromine hydrolysis equilibrium is maintained during the reaction, we may write for the rate of reaction

$$dx/dt = K'_2\,(A - x)(B - x)/(C + 2x)^2(D + 2x) \tag{16}$$

Integrating this expression and eliminating the constant, we obtain

$$\tau K'_2 = 4x^2 + Ex + F \ln \frac{B}{(B - x)} - G \ln \frac{A}{(A - x)} \tag{17}$$

where $E = 8(A + B + C + D/2)$,
$F = (B^2E - 8AB^2 + 4BCD + 2BC^2 + C^2D)/(A - B)$, and
$G = (A^2E - 8A^2B + 4ACD + 2AC^2 + C^2D)/(A - B)$

Four experiments at widely varying acid concentration were chosen to test this formula. The results of these computations are given in Table III.

TABLE III

COMPARISON OF SPECIFIC REACTION RATES BASED ON THE HYPOBROMITE ION AND HYPOBROMOUS ACID MECHANISMS

Expt. no., Table I	(H^+)	$K'_2 \times 10^4$	$K_a \times 10^2$
8	0.00063	1.8	2.1
12	.0126	4.2	2.4
18	.380	140	3.7
19	.585	188	3.0

The second column lists the initial acid concentrations; the third the values of K'_2 (Equation 17); and the fourth the values of the constant of Equation 10 (or 9) taken from Table I. These data demonstrate clearly that Equation 17 (and therefore Equation 15) does not fit the facts.

Summary

1. A convenient method is presented for measuring reaction velocities having half times of the order of magnitude of one second.

2. The rate of reduction of bromine by hydrogen peroxide is shown to conform to the equation

$$-d(H_2O_2)/dt = \chi_2(H_2O_2)(Br_2)/(H^+)(Br^-)\gamma^2_{HBr}$$

even in solutions in which the concentrations of acid and bromide are very small. At 25 and 35° the values of χ_2 are 0.018 and 0.043, respectively, when concentrations are expressed in moles per liter and times in minutes.

3. This equation and the value of χ_2 at 25° are concordant with, and

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[23] Cf. ref. 1, p. 1264. In several of the rate experiments performed at high acid concentration, analytical evidence was obtained for the existence of small quantities of an oxidizing agent having the properties of bromate ion.

were predicted from, experimental data on the catalytic decomposition of hydrogen peroxide.

4. Balint's earlier measurements at 0°, which hitherto have been overlooked, are summarized. When the activity correction is applied χ_2 is equal to 0.00062.

5. The hypobromite ion mechanism suggested by Christiansen is shown to be unsatisfactory.

6. The hypobromous acid mechanism for the reaction between hydrogen peroxide and bromine and for the catalytic decomposition of hydrogen peroxide is in excellent agreement with the known experimental facts.

7. A satisfactory iodimetric method of determining hydrogen peroxide is described.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 212]

THE REDUCTION POTENTIAL OF SELENOUS ACID AND THE FREE ENERGY OF AQUEOUS SELENIC ACID

BY M. S. SHERRILL AND E. F. IZARD

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Introduction

It is well known that selenic acid may be prepared by oxidizing an aqueous solution of selenous acid with chlorine, and that selenic acid may be reduced to selenous acid by treatment with concentrated hydrochloric acid. This at once leads to the conclusion that, for the reaction $Cl_2 + H_2SeO_3 + H_2O = H_2SeO_4 + 2HCl$, there should be a concentration of hydrochloric acid at which a measurable amount of both selenic and selenous acids would be present when the pressure of chlorine is approximately one atmosphere.

The equilibrium conditions of this reaction were investigated for the purpose of determining, with the aid of the known chloride–chlorine potential, the reduction potential of the reaction H_2SeO_3 (1 m.) $+ H_2O =$ $HSeO_4^-$ (1 m.) $+ 3H^+$ (1 m.) $+ 2E^-$. The thermodynamic relations involved are indicated below.

The reaction, written in the ionic form Cl_2 (g) $+ H_2O + H_2SeO_3 =$ $3H^+ + HSeO_4^- + 2Cl^-$ takes place in the hypothetical voltaic cell

$$\mathrm{Pt}\left\{\begin{matrix} H_2SeO_3\ (1\ \mathrm{m.}) \\ HSeO_4^-\ (1\ \mathrm{m.}) \\ H^+\ (1\ \mathrm{m.}) \end{matrix}\right\} \| \ Cl^-\ (1\ \mathrm{m.}),\ Cl_2\ (1\ \mathrm{atm.}) + \mathrm{Pt}$$

The free energy decrease ($-\Delta F$) attending the change in state in this cell, corresponding to the passage of two faradays, may be calculated either from the electromotive force E of the cell, or from the equilibrium constant K of the reaction by the following well-known equations

$$-\Delta F = 2\mathrm{E}F = RT \ln K$$

The total electromotive force E is, however, equal to the difference $E_1 - E_2$ between the two separate electrode potentials. Since the chloride–chlorine potential E_2 is known at 25° to be equal to -1.359 volt,[1] the desired reduction potential E_1 is given by the equation

$$E_1 = -1.359 + \frac{RT}{2F} \ln K = -1.359 + 0.02957 \log K$$

In order to verify the value of E_1 obtained in this way a study was also made of the corresponding oxidation-reduction reaction with bromine and hydrobromic acid in place of chlorine and hydrochloric acid. In this investigation the activity and concentration of the bromine in the equilibrium solution was conveniently regulated and determined by distribution into carbon tetrachloride. The thermodynamic relations involved are the same as those above. In this case the reduction potential E_1 was calculated by the equation

$$E_1 = -1.087 + 0.02957 \log K$$

in which -1.087 volts[2] is the potential of the bromide–bromine electrode at 25°.

Preparation and Purification of the Chemicals

The chemicals used are listed below, together with the method of preparation or purification.

Selenous Acid.—At the start of the work a small amount of C. P. crystalline selenous acid which had been obtained from the General Chemical Company was available. It was further purified by recrystallizing from water several times. After this supply was exhausted the acid was prepared from a sample of commercial selenium. The method used was that suggested by Dennis and Koller,[3] which consists of dissolving the selenium in nitric acid, evaporating to dryness several times with water to remove the nitric acid, then recrystallizing the resulting acid from water four times. A very pure sample of selenous acid may be obtained in this way.

Selenic Acid.—At first a small amount of selenic acid solution (approx. 43%) obtained from the General Chemical Company was also available. Later the acid was prepared from the purified selenous acid, using the method suggested by Meyer and Moldenhauer,[4] which consists in oxidizing the selenous acid to selenic acid by means of chloric acid, prepared from barium chlorate, and then concentrating the resulting solution in *vacuo*. An 85% acid prepared in this way showed the presence of only a trace of selenous acid.

Chlorine.—The chlorine was prepared by dropping concentrated hydrochloric acid on C. P. potassium permanganate in a glass generating flask. The resulting chlorine was washed by passing it through a solution of hydrochloric acid of approximately the same concentration as the acid in the equilibrium chamber.

Hydrochloric Acid.—All solutions were made up from C. P. concentrated hydrochloric acid of specific gravity 1.19.

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[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923, p. 426.

[2] Lewis and Randall, Ref. 1, p. 427.

[3] Dennis and Koller, THIS JOURNAL, 41, 949–970 (1919).

[4] Meyer and Moldenhauer, *Z. anorg. Chem.*, 116, 193–200 (1921).

Bromine.—U. S. P. bromine was further purified by allowing it to stand for several days over finely powdered, recrystallized potassium bromide and then distilling in an all glass apparatus. The middle portion of the distillate (about one-third of the total) was then used.

Hydrobromic Acid.—All solutions were made up from C. P. constant boiling **hydrobromic** acid prepared in the usual way.

Carbon Tetrachloride.—Eastman's C. P. sulfur-free carbon tetrachloride was refluxed with bromine for six hours in an all glass apparatus. The bromine was removed by repeated washing with dilute sodium hydroxide and finally with water. The product was then dried over anhydrous calcium chloride for two weeks and distilled. The fraction boiling between 76.71 and 76.81° was used.

Preparation of the Equilibrium Mixtures

Chlorine System.—Merewether[5] has shown that when selenic acid is dissolved in 2.06 N hydrochloric acid and the solution saturated with chlorine at room temperature, no selenous acid can be detected even after long standing; also that when selenous acid is dissolved in 12 N hydrochloric acid and the solution saturated with chlorine no selenic acid is formed. However, he found measurable quantities of both selenic and selenous acids present in a solution from 7–9 molal in hydrochloric acid with a chlorine pressure of one atmosphere. In view of these facts the present work was carried out with solutions ranging from 7–8.5 molal in hydrochloric acid and the chlorine pressure between 650 and 900 mm.

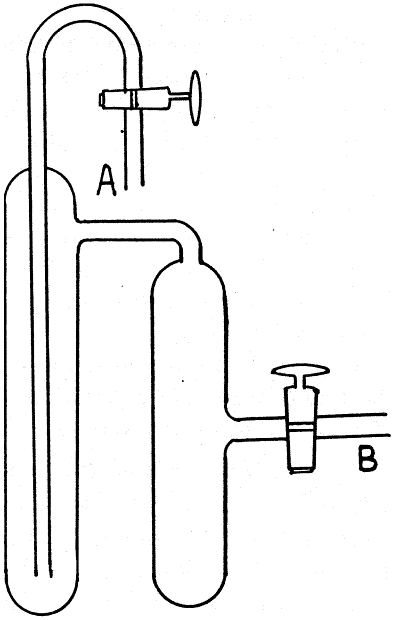

Fig. 1.

The hydrochloric acid solution, containing in some cases selenic acid, in other cases selenous acid and in still other cases both selenic and selenous acids, was placed in the glass apparatus shown in the figure. Chlorine, prepared as previously described, was then bubbled through the solution until all air was expelled and the solution saturated with the gas at a pressure somewhat greater than one atmosphere. The apparatus was then placed in a horizontal position in a thermostat at 25.00 ± 0.01° and gently rocked until equilibrium was reached. In most cases the chlorine pressure was adjusted so that at equilibrium the pressure would be approximately one atmosphere. In other cases the pressure was allowed to adjust itself and was measured by means of a mercury manometer. With a manometer

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[5] Merewether, M. I. T. Thesis, 1925, unpublished.

connected to the apparatus it served as a fairly delicate method of indicating when equilibrium had been reached. When there was no further change in pressure the apparatus was shaken for twelve to twenty-four hours longer to insure equilibrium. By applying pressure to the apparatus at B, the solution was forced out at A, directly into the weighing bottle. Weighed samples were then analyzed for the various constituents.

No attempt was made to determine the rate of the reaction in either direction, but from the length of time (four to seven days) necessary to establish equilibrium it is known to be very slow.

Bromine System.—The reduction potential obtained in the chlorine system indicated that the equilibrium constant in a bromine system should be near unity. Since the bromine concentration could be kept low, this meant that the concentration of hydrobromic acid could be kept below one molal.

Equilibrium was established in the system in the following way: about 40 cc. of a solution of bromine in carbon tetrachloride (mole fraction 0.0005–0.005) was placed in a glass-stoppered cylinder of 100cc. capacity; then about 60 cc. of a hydrobromic acid solution (molality 0.10–0.40) containing either selenous acid or selenic acid, and in some cases both selenous and selenic acid, was added. The cylinder was stoppered and sealed with paraffin, placed in a thermostat at 25.00 ± 0.01° and shaken until equilibrium was established. The water layer was then analyzed for hydrobromic, selenous and selenic acids and the carbon tetrachloride layer for bromine.

As in the chlorine system no attempt was made to determine the rate of the reaction in either direction, but it must be extremely slow since from fifty to seventy days were necessary for equilibrium to be established.

Methods of Analysis of the Equilibrium Mixtures

The concentrations of hydrochloric, hydrobromic, selenous and selenic acids and that of chlorine and bromine in the equilibrium mixtures were determined as follows.

Hydrochloric Acid.—A weighed sample was diluted with ice water and shaken over mercury for thirty minutes to remove the chlorine. The mercury was then removed with a separatory funnel and the mercurous chloride by filtration. The hydrochloric acid in the filtrate was determined by the silver thiocyanate method, as modified by Drecksel.[6]

Selenous Acid.—A weighed sample was diluted with ice water and chlorine or bromine removed as before. The selenous acid was then determined by the method of Norris and Fay,[7] which is based on the reaction

$$SeO_2 + 4HCl + 4Na_2S_2O_3 \longrightarrow Na_2S_4SeO_6 + Na_2S_4O_6 + 4NaCl + 2H_2O$$

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[6] See Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1914, p. 707.

[7] Norris and Fay, *Am. Chem. J.*, **23**, 119–128 **(1900).**

The solution (usually about 200 cc.) was cooled to 0°; then, after addition of 10 cc. of concentrated hydrochloric acid, sodium thiosulfate was added in slight excess, this excess being titrated with iodine, using starch as indicator.

Selenic Acid.—A weighed sample was placed in a long-necked, round-bottomed flask of 250cc. capacity, 75 cc. of concentrated hydrochloric acid added and the mixture refluxed on a water-bath for eight to ten hours, using a glass tube placed inside the neck of the flask as a condenser. The solution was then cooled to 0° and the selenous acid determined as before. The selenic acid was determined by difference.

It is known that in hot solution hydrochloric acid and selenous acid react to form selenium tetrachloride and that some of the tetrachloride escapes with the vapors. However, it was found by very careful experimentation that with the system of refluxing used no selenium was lost, even after long boiling.

Chlorine.—Although the activity of the chlorine in the equilibrium mixture is definitely determined by the pressure of the chlorine, it was nevertheless necessary to determine the amount of dissolved chlorine in order to compute the concentrations of the other substances as formula weights per 1000 g. of water. As no method presented itself for the direct determination of chlorine in the presence of selenous acid, these concentrations of chlorine were obtained by graphical interpolation from the values given in the following section for the solubility of chlorine in hydrochloric acid of varying composition. In these hydrochloric acid solutions the chlorine was determined by titrating a weighed sample, after addition of potassium iodide, with sodium thiosulfate.

Hydrobromic Acid.—A weighed sample was diluted with water and the bromine removed by shaking with mercury under conditions previously described for removing chlorine. The hydrobromic acid in the filtrate was then determined by the silver thiocyanate method.

Bromine.—A weighed sample of the carbon tetrachloride layer was added to potassium iodide and the liberated iodine titrated with sodium thiosulfate. The total bromine in the hydrobromic acid solutions was determined by titrating a weighed sample of the aqueous layer, after addition of potassium iodide, with sodium thiosulfate.

Solubility of Chlorine in Hydrochloric Acid Solutions

Jakowkin[8] has shown that chlorine is more soluble in hydrochloric acid solutions than in pure water. He attributed the increase in solubility to the reaction, $Cl_2 + Cl^- = Cl_3^-$. As his results do not cover the range of concentrations needed in this investigation, it was necessary to make a series of direct determinations of the solubility of chlorine in solutions of

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[8] **Jakowkin,** *Z. physik. Chem.,* **29, 613** (1899).

hydrochloric acid, not only to find the total amount of dissolved chlorine in the equilibrium mixtures, but also to be able to estimate the proportion of chloride in such mixtures converted to trichloride ion. The equilibrium was established as described above for the cases in which selenic and selenous acids were also present.

The results of these solubility determinations are given in Table I. The solubility of chlorine was reduced to the basis of one atmosphere pressure of chlorine gas by applying Henry's law, which is valid over the narrow range of pressure involved. The partial pressure of chlorine saturating the solution was found by deducting from the observed barometric pressure the sum of the partial vapor pressures of water and of hydrochloric acid in the solution. The latter were obtained from vapor-pressure measurements of hydrochloric acid solutions containing no dissolved chlorine. As no direct determinations of the total vapor pressure of such solutions were available, it was necessary to combine Dobson and Masson's[9] measurements of the partial vapor pressure of water with Bates and Kirschman's[10] measurements of the partial vapor pressure of hydrochloric acid in solutions of varying acid content. The desired values for the total vapor pressure were obtained from these measurements by graphical interpolation.

TABLE I

SOLUBILITY OF CHLORINE GAS IN HYDROCHLORIC ACID AT 25° AND ONE ATMOSPHERE

	Concentration of			Ratio
ΣHCl	ΣCl_2	(Cl_3^-)	(Cl^-)	$(Cl_3^-)/(Cl^-)$
4 903	0 0978	0.0360	4 867	0.00739
7.016	.1150	.0532	6 963	,00764
8.163	.1219	.0601	8.102	,00742
8 854	.1281	.0663	8 788	.00754
9.806	.1326	.0709	9.734	.00727

The concentrations in the table are expressed as formula weights (or moles of the molecular species) per 1000 g. of water. The concentration of the trichloride ion in the third column was computed under the assumption that the acids are completely ionized and that the concentration of Cl_2 as such is 0.0618 *M*, the value derived by Lewis and Randall[11] from Jakowkin's data for this saturation concentration in dilute aqueous solutions when the (partial) pressure of Cl_2 is 1 atm. Under this assumption, the ratio $(Cl_3^-)/(Cl^-)$ given in the last column corresponds to the equilibrium constant of the reaction $Cl_2\ (g) + Cl^- = Cl_3^-$. In consideration of the fact that the actual solubility of the molecular species Cl_2 is almost certainly less than the assumed value (0.0618M), the value of the constant is to be regarded only as a rough approximation. Its average value

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[9] Dobson and Masson, J. *Chem. Soc.*, **125, 668 (1924).**

[10] Bates and Kirschman, THIS JOURNAL, 41, 1991 **(1919).**

[11] **Ref. 1, p.** 502.

(0.0074) was used to compute the small proportion of chloride converted to trichloride in the equilibrium mixtures containing selenous and selenic acids. The value evidently corresponds to 0.74% conversion at all concentrations of hydrochloric acid.

Distribution of Bromine between Carbon Tetrachloride and Aqueous Solutions of Hydrobromic Acid

Jakowkin,[12] and Lewis and Storch[13] have shown from the distribution of bromine between carbon tetrachloride and aqueous solutions of potassium bromide or hydrobromic acid that bromine dissolved in the aqueous layer is partly converted to *a* tribromide ion by the reaction $Br_2 + Br^- = Br_3^-$. Lewis and Storch have computed the equilibrium constant of this reaction to be approximately 16.4 at 25°, which does not differ greatly from the value obtained by Jakowkin. As their measurements were limited to a single concentration of acid, 0.1 formal HBr, it seemed desirable to make a series of determinations at varying acid concentrations. The results are shown in Table II.

The equilibrium conditions were established and analyses made by the methods described in the preceding section. The total concentration of bromine, given in Col. 2, was kept low in order to reduce the tendency to form a pentabromide, or higher bromide ion.

TABLE II

EQUILIBRIUM CONCENTRATIONS IN SOLUTIONS OF HYDROBROMIC ACID AND BROMINE AT 25°

Formula weights per 1000 g. of water			Molality		
ΣHBr	ΣBr_2	(Br_2)	(Br_3^-)	(Br^-)	$K = \frac{(Br_3^-)}{(Br_2)\ (Br^-)}$
0.10408	0.0018675	0.0006847	0.001183	0.10290	16.80
.10408	.003290	.001209	.002081	.10200	16.87
.10408	.004303	.001591	.002712	.10137	16.81
.10408	.006467	.002406	.004061	.10002	16.88
.3216	.004944	.0007671	.004177	.31747	17.15
.4408	.01578	.001867	.01391	.4269	17.45
.4408	.02172	.002594	.01913	.4217	17.48
.5204	.01779	.001799	.01599	.5044	17.62
.5204	.03855	.00404	.03451	.4859	17.58

The molality of bromine recorded in the third column was calculated from the analysis of the tetrachloride layer with the aid of the distribution ratio of bromine between water and carbon tetrachloride given by Lewis and Storch. In dilute solution this ratio is $c/x = 0.371$, where c is the molality of bromine in the water solution and x is its mole fraction in the tetrachloride solution.

The values of the equilibrium constant shown in the last column are all somewhat higher than the value given by Lewis and Storch, and increase

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[12] Jakowkin, *Z. physik. Chem.*, 18, 583 (1895); 20, 19 (1896).

[13] Lewis and Storch, THIS JOURNAL, 39, 2544 (1917).

with increasing concentration of the hydrobromic acid. In computing the amount of bromide converted to tribromide ion in the equilibrium mixtures containing selenous and selenic acids, a value of the equilibrium constant was chosen which corresponded to the total concentration of hydrobromic acid present.

Tabulation and Discussion of Results

Chlorine System.—The values given in Cols. 2 to 5 of Table III represent the total concentrations of the respective substances as determined from the analyses and from graphical interpolation of the solubility data for chlorine. Ratios (p/p_0) of the vapor pressure of water in the solutions to the vapor pressure of pure water are recorded in the seventh column as the activity $[H_2O]$ of water. The values for the molality of the hydrogen ion and that of the chloride ion were computed from the total concentration of acid under the assumption that hydrochloric acid, and selenic acid, with respect to its first hydrogen, are completely ionized, and that selenous acid, and selenic acid, with respect to its second hydrogen, are in these solutions of high hydrogen ion activity un-ionized. In computing the chloride ion concentration a correction was made for the small proportion of chloride converted to trichloride.

TABLE III

COMPOSITION OF THE EQUILIBRIUM MIXTURES AT 25°

	Formula weights per 1000 g. of water				Pressure	Activity	Molality of		Ion	Con-	Reduction
Expt.	ΣHCl	ΣCl_2	H_2SeO_4	H_2SeO_3	atm. of Cl_2,	of water $[H_2O]$	(H^+)	(Cl^-)	activation (γ)	stant, $K \times 10^{-9}$	potential, E_1
1[a]	6.886	0.1118	0.2380	0.0467	1.000	0.5921	7.124	6.836	4.554	1.297	−1.0899
2[a]	7.412	.11346	,2310	.1813	.9784	.5577	7.643	7.539	5.314	1.272	−1.0902
3[a]	7.623	,11587	,1003	.1014	.9849	.5530	7.723	7.568	5.440	1.242	−1.0905
4	7.68%	.11511	.0723	.0777	.9823	.5513	7.754	7.627	5.491	1.274	−1.0902
5[a]	7.706	,11691	,1821	.2156	.9856	.5429	7.888	7.650	5.71	1.571	−1.0875
6[a]	7.836	,12472	,1018	.1636	1,0473	,5400	7.938	7.776	5.805	1.273	−1.0902
7	7.132	.11166	.8342	.9510	0.9815	,5379	7.966	7.081	5.84	1.595	−1.0873
8[a]	7.854	,14965	,1199	.1688	1.2565	,5370	7.974	7.782	5.85	1.295	−1.0900
9[a]	7.981	,09937	,0837	.1982	0.8312	.5311	8.065	7.981	5.91	1.346	−1.0895
10	8.374	,12001	.0612	,3009	.9710	5093	8.435	8 314	6.725	1.615	−1.0871
11	8.447	.12182	,0719	.3761	,9842	,5034	8.519	8.386	6.90	1.81	−1.0857
									Mean	1.42	1.088

[a] Equilibrium approached from the chlorine side.

The equilibrium constant was calculated under the assumption that the mean activity coefficient of selenic acid (regarded here as a univalent acid) is the same as that of hydrochloric acid. The values employed in the calculation are tabulated in Col. 10. They were taken equal to the mean activity coefficient of hydrochloric acid as given by Randall and Young[14] at a concentration equal to that of (H^+) in the equilibrium mixture. Under these assumptions the equilibrium constant is given by the equation

$$K = \frac{(H^+)^3(HSeO_4^-)(Cl^-)^2\gamma^6}{(H_2SeO_3)\ [H_2O]\ p_{Cl_2}}$$

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

In the last two columns of the table are recorded the value of this constant, and the corresponding values for the reduction potential E_1 of the reaction H_2SeO_3 (1 m.) + H_2O = $3H^+$ (1 m.) + $HSeO_4^-$ (1 m.) + $2E^-$ computed by the equation previously given. The error in the equilibrium constant due to the assumptions that H_2SeO_3 and $HSeO_4^-$ are not appreciably ionized is probably very small. It can be shown to be so in the case of selenous acid by reference to its ionization constant, which is given by Blanc[15] to be equal to 0.0027.

The ionization relations of selenic acid are not definitely known, but are almost certainly similar to those of sulfuric acid. This is indicated not only by its chemical behavior but also by the fact that the change in its equivalent conductance with concentration closely parallels that of sulfuric acid.[16] Furthermore Small[17] has shown that the electromotive force of a voltaic cell of the type H_2, H_2SO_4 (c. f.), H_2SeO_4 (c. f.), H_2 is substantially zero, when the concentrations of the two acids in the cell are made equal to each other. (It was not possible to carry such measurements to concentrations above 1.0 f, since at these higher concentrations reduction to selenium takes place at the platinized electrode.)

Sherrill and Noyes[18] have derived the value 0.0115 for the ionization constant of the second hydrogen of sulfuric acid under the assumption that the first hydrogen is completely ionized. Adopting this same value as the ionization constant of the $HSeO_4^-$, the ratio $[SeO_4^=]/[HSeO_4^-]$ of the activity of $SeO_4^=$-ion to that of $HSeO_4^-$-ion in the equilibrium mixtures may be computed from the activities of the H^+-ion. Thus in Expt. 1, $[SeO_4^=]/[HSeO_4^-] = 0.0115/32.4 = 0.00035$. The small values thus obtained for these activity ratios make plausible the assumption that the concentration of $SeO_4^=$-ion is negligibly small in comparison with that of the $HSeO_4^-$-ion.

The assumption that the mean activity coefficient of selenic acid is equal to that of hydrochloric acid is not exact but is the simplest assumption to make under the circumstances.

The mean values for the equilibrium constant and for the reduction potential obtained are 1.4×10^9 and -1.088 volts, respectively.

Bromine System.—The concentrations of the various substances present in the aqueous solution at equilibrium are given in Table IV. The ion activation values in Col. 9 were taken equal to the mean activity coefficient of hydrobromic acid, as given by Livingston,[19] at a concentration equal to the total hydrogen ion concentration recorded in Col. 7. The

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[15] Blanc, J. *chim. phys.*, **18**, 28 (1920).

[16] Landolt-Bornstein, "Phys Chem. Tabellen," pp. 1081 and 1093.

[17] Small, M. I. T. *Thesis, 1927.*

[18] Sherrill and Noyes, THIS JOURNAL, 48, 1861 (1920).

[19] Livingston, *ibid.*, **48**, 45 (1920).

TABLE IV

COMPOSITION OF THE EQUILIBRIUM MIXTURES AT 25°

	Formula weights per 1000 g. of water				Molality			Ion-Activation (γ)	Constant K	Reduction potential E_1
Expt.	ΣHBr	ΣBr_2	H_2SeO_4	H_2SeO_3	(Br_2)	(H^+)	(Br^-)			
1	0.1725	0.0005233	0.08547	0.08475	0.0001333	0.2579	0.1721	0.7887	0.944	-1.0877
2"	.2779	.001520	.03244	.07493	.0002802	.3104	.2767	.7865	.837	-1.0892
3"	.2875	.001551	.02647	.05876	.0003016	.3120	.2860	.7864	.878	-1.0887
4	.2955	.001390	.02821	.09460	.0002302	.3237	,2943	.7862	.899	-1.0884
5"	.1059	.002593	.2225	.02669	.0009334	.3284	.1042	.7861	.810	-1.0897
6[a]	.2362	.002999	.09511	.06818	.0006992	.3315	.2339	.7861	.938	-1.0878
7[a]	.2445	.004176	.1158	.1026	.0008169	.3603	.2411	,7863	.888	-1.0885
8	.2952	.005557	.08447	.1158	.000927	.3797	.2906	.7863	.860	-1 0889
9[a]	.1860	.002347	.1966	.1922	.0005674	.3824	,1841	.7864	.808	-1.0897
10	.3047	.005747	.08334	.1166	.000947	.3880	.2999	.7870	.942	-1.0878
								Mean	.88	-1.088

[a] Equilibrium approached from the bromine side.

values of the equilibrium constant tabulated in Col. 10 were calculated under assumptions entirely analogous to those made in the case of the chlorine equilibrium except that in these more dilute solutions the activity of water was taken equal to unity. The values for the equilibrium constant were thus calculated by the equation $K = \dfrac{(H^+)^3(HSeO_4^-)(Br^-)^2\gamma^6}{(H_2SeO_3)(Br_2)}$

The assumption that H_2SeO_3 and $HSeO_4^-$ are not appreciably ionized is less justified here than in the case previously considered. It may, however, be noted that, since the ratio of the concentration of these two substances occurs in the expression of the equilibrium constant, there is a tendency for the two errors introduced by the assumption to counterbalance each other.

The mean values for the equilibrium constant and the reduction potential are **0.88** and **-1.088** volts, respectively. It is fortuitous that this value for the reduction potential is identical with that obtained from a study of the chlorine equilibrium, considering the approximate assumptions that were necessarily made.

The Free Energy of Aqueous Selenic Acid

From the value of the reduction potential (-1.088 volts) the free energy decrease attending the corresponding change in state may be calculated by the familiar equation $-\Delta F = ENF$. The result is shown by the following free energy equation

$$H_2SeO_3 + H_2O(l) = H^+ + HSeO_4^- + H_2(g) - 50210 \text{ cal.} \qquad (1)$$

According to Schott, Swift and Yost,[20] at 25°

$$Se(s) + \frac{3}{2} O_2(g) + H_2(g) = H_2SeO_3 + 101360 \text{ cal.} \qquad (2)$$

According to Lewis and Randall,[21] at 25°

$$H_2(g) + \frac{1}{2} O_2(g) = H_2O\ (l) + 56560 \text{ cal.} \qquad (3)$$

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[20] Schott, Swift and Yost, THIS JOURNAL, 50, 721 (1928).

[21] Ref. 1, p. 485.

By addition of these three free energy equations there results

$$Se(s) + 2\,O_2(g) + H_2(g) = H^+ + HSeO_4^- + 107710 \text{ cal.} \qquad (4)$$

That is, $\Delta F_{298} = -107710$ cal. for $HSeO_4^-$ (or for one formula weight of aqueous H_2SeO_4).

Summary

The equilibrium conditions of the reactions

$$Cl_2(g) + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Cl^- \quad \text{and}$$
$$Br_2 + H_2SeO_3 + H_2O = 3H^+ + HSeO_4^- + 2Br^-$$

were determined at 25°. The values of the corresponding equilibrium constants were found to be 1.42×10^9 and 0.88, respectively. From each of these constants and known thermodynamic data the reduction potential of the reaction $H_2SeO_3 + H_2O\ (l) = 3H^+ + HSeO_4^- + 2E^-$ was calculated to be -1.088 volts. From this value and existing free energy data, the free energy (ΔF) at 25° of $HSeO_4^-$ (or of one formula weight of aqueous H_2SeO_4) was calculated to be $-107{,}710$ cal.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

APPLICATIONS OF CERIC SULFATE IN VOLUMETRIC ANALYSIS. IV. THE POTENTIOMETRIC TITRATION OF VANADYL ION ALONE OR IN THE PRESENCE OF FERRIC AND CHROMIC IONS. NOTE ON THE STABILITY OF VANADYL SOLUTIONS[1]

BY N. HOWELL FURMAN

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This communication reports further progress in a study of the direct uses of standard ceric sulfate solutions in volumetric analysis. The apparatus and technique have been described in a former paper.[2]

Experimental

Approximately 0.05 M solutions of ceric sulfate in dilute sulfuric acid were prepared and standardized by potentiometric titration with oxalic acid (exactly 0.05 N) that had been prepared by dissolving pure, dry sodium oxalate in water acidified with 10 cc. of sulfuric acid (sp. gr. 1.84) per liter.

Note on the Stability of Vanadyl Solutions.—During the course of the investigation observations were made on the stability of vanadyl solutions. The author's findings are in agreement with the conclusions of Stout and Whitaker[3] who stated that vanadyl solutions are stable for six months or more.

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[1] Presented at the spring meeting of the American Chemical Society at St. Louis, Missouri, April, 1928.

[2] Furman, THIS JOURNAL, **50**, 755 (1928).

[3] Stout and Whitaker, *Ind. Eng. Chem.*, **20**, 210 (1928).

Portions of ammonium metavanadate of C.P. grade weighing between 11.7 and 13.8 g. were dissolved in sulfuric acid (30 cc. of concd. acid of sp. gr. 1.84 and about 100 cc. of water). After reduction each solution was diluted to 2 liters. Two methods of reduction to the vanadyl state were employed: (a) the familiar sulfur dioxide method for the preparation of solutions free from chloride;[4] and (b) reduction by shaking with mercury after the addition of 13 cc. of hydrogen chloride of sp. gr. 1.18–1.19.[5]

Weighed portions of the vanadyl solutions were titrated with potassium permanganate which had been standardized against pure sodium oxalatr. All end-points were determined potentiometrically.[6] The stability of the vanadyl solutions is evident from the following figures, which are in each instance averages of two concordant determinations.

STABILITY OF VANADYL SULFATE SOLUTIONS

Time, weeks ...	0	2	5	8	15	65
Normality......	0 05739	0.05740	0.05737	0.05740	0.05730	0.05730

The solution that contained hydrochloric acid was equally stable. At the outset its normality was 0.05695 and after sixty-five weeks the value was 0.05683. The solutions were in clear glass bottles that were exposed to diffuse sunlight for six months; during the balance of the period the solutions were in a dark cupboard. A 0.04914 *N* solution free of chloride was used in a portion of the work that was done in Zürich, Switzerland.

Potentiometric Study of the Ceric–Vanadyl Reaction

Measured portions of the vanadyl solutions were titrated with ceric sulfate. All end-points were determined potentiometrically, using a burnished platinum spiral (No. 28 B. and S. gage wire) 6–8 cm. long as indicator electrode and a N calomel half-cell as reference electrode. The platinum wire was immersed in chromic acid cleaning solution when not in use. Accurate results are obtained when the vanadyl solution is at room temperature, but it requires several minutes for the potential to become constant in the neighborhood of the end-point. At temperatures between 50 and 60° the rate of reaction is rapid and the titration is as satisfactory as the permanganate titration is at 80°. The break in potential at the end-point per 0.05 cc. of 0.03 *N* ceric solution amounts to 0.025 to 0.1 volt when the initial volume of the solution lies between 200 and 25 cc. Typical titration graphs are shown in Fig. 1, Curves 1 and 2. Representative results are presented in the following table.

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[4] For details see Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, 1919, 5th ed , Vol. II, p. 636.

[5] Method of McCay and Anderson, THIS JOURNAL, 44, 1018 (1922).

[6] A summary of the literature relating to the potentiometric titration of vanadium is to be found on p. 244 of "Potentiometric Titrations," Kolthoff and Furman, published by John Wiley and Sons, Inc., New York.

TABLE I

POTENTIOMETRIC TITRATION OF VANADYL SOLUTIONS WITH CERIC SULFATE

A. Reaction at room temperature. 0.05735 N vanadyl and 0.0547 N ceric solution

Vanadyl soln., cc.	25	25	10	10	25
Ceric soln. used, cc. ..	26.15	26 19	10.48	10.49	26 22
Ceric soln. calcd., cc.. .	26.21	26 21	10.48	10 48	26 21

B. Reaction at 50–60°. Nos. 1–4, vanadyl sulfate 0.04914 N, ceric solution 0.05655 *N*. Nos. 5–6, vanadyl chloride 0.05683 N, ceric solution 0.05455 N

	1	2	3	4	5	6
Vanadyl soln., cc	25	25	25	50	25	25
Ceric soln. used, cc .	21 73	21 70	21 68	43 39	26 03	26 06
Ccric soln. calcd, cc..	21.71	21 71	21 71	43 42	26 05	26 0.5

C. Reaction at 50–60°. Trivalent iron and chromium present. Nos. 1–3, 0.04914 N vanadyl sulfate, 0.05655 N ceric. Nos. 4–6, 0.05735 N vanadyl sulfate, 0.04824 *N* ceric. Nos. 7–8, 0.05683 N vanadyl chloride, 0.04824 N ceric

	1	2	3	4	5	6	7	8
Vanadyl soln., cc......	25	25	50	25	25	10	25	10
Ceric soln. used, cc....	21.73	21.71	43.46	29.70	29.75	11.87	29.51	11.76
Ceric soln. calcd., cc...	21.71	21.71	43.42	29.71	29.71	11.89	29.45	11.78
Iron present, g........	0.14	0.14	1.64	1.14	2.28	1.14	1.14	1.14
Chromium present, g..	.086	.086	0.086	0.35	0.70	0.35	0.35	0.35

The initial volumes ranged from 23 to 123 cc. Near the end-points the ceric solution was added in drops that averaged 0.025 cc. Chromic solutions were prepared by exact reduction of bichromate with ferrous sulfate (potentiometric end-point). It was found possible to control the process of reduction of a large quantity of bichromate so exactly that 50 cc. of the reduced solution (containing 1.14 g. of iron and 0.35 g. of chromium) when treated with one drop of 0.05 *N* ferrous sulfate showed a change of 0.05 volt in oxidation-reduction potential; with one drop of 0.05 *N* ceric solution there was a rise of 0.2 volt.

At temperatures between 50 and 60° vanadyl salts are, therefore, selectively oxidized by ceric sulfate in the presence of large quantities of both chromic and ferric salts. Under these conditions the titration graph is not appreciably modified (see Curve **3,** Fig. 1).

The small quantities of hydrochloric acid that were present in one of the vanadyl solutions were without influence upon the accuracy of the method.[7]

Simultaneous Determination of Iron and Vanadium.—The titration of mixtures of ferrous and vanadyl solutions was studied because this problem enters into most of the practical methods for the determination of

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[7] While this article was in preparation the author saw in manuscript, papers by H. H. Willard and Philena Young. These investigators have also studied the use of ceric sulfate as a volumetric reagent and have made a study of the effect of large quantities of hydrochloric acid in certain titrations. It would appear from their results that even very large quantities of hydrochloric acid are without effect. The author has not studied this question in detail, but found in one titration that 10 cc. of concd. HCl (sp. gr, 1.18-1.19) per 100 cc. did not cause any error in the titration of a vanadyl solution.

vanadium in natural and synthetic products. Measured quantities of ferrous and vanadyl solutions were mixed and titrated potentiometrically with ceric solution. The first inflection (complete oxidation of iron) was determined at room temperature.[8] The solution was heated to 50–60° and the titration was continued until the end-point of the oxidation of the vanadyl salts was found. The results are accurate for both iron and vanadium. Curves 4 and 5, Fig. 1, are representative titration graphs.

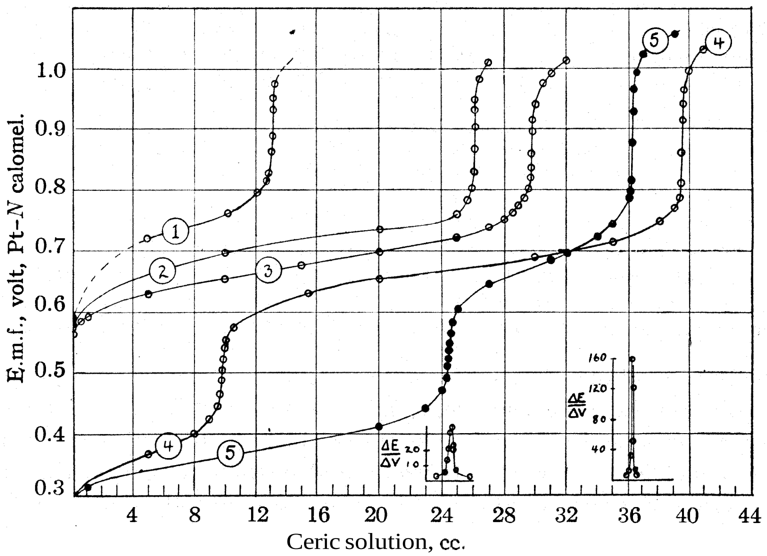

Fig. 1.—Titration of vanadyl and ferrous solutions with ceric sulfate. Curve 1, 25 cc. and Curve 2, 50 cc. of 0.05735 N vanadyl sulfate titrated with 0.1092 N ceric solution. Curve 3, 25 cc. of 0.05735 N vanadyl solution mixed with 100 cc. of a solution containing 2.28 g. of iron and 0.7 g. of chromium and titrated with 0.04824 N ceric solution. Curve 4, 10 cc. of 0.04724 N ferrous and 25 cc. of 0.05735 N vanadyl sulfate titrated with 0.04824 N ceric solution. Curve 5, 25 cc. of 0.04764 N ferrous and 10 cc. of 0.05683 N vanadyl chloride solution titrated with 0.04857 N ceric solution. (Values for $\Delta E/\Delta V$ have been multiplied by 100 in constructing the graph.)

It was found advisable to plot the difference quotient ($\Delta E/\Delta V$ where ΔE is the e.m.f. difference per amount of reagent ΔV) against cc. of reagent in order to determine the first inflection. The second inflection is so sharp that it is rarely necessary to plot the values. The results are assembled in Table II.

As a further test of the accuracy of the titration with ceric sulfate of vanadyl salts in the presence of iron, chromium and other components of

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[8] E. Müller and A. Flath, Z. *Elektrochem.*, 29, 500 (1923), found that the inflection was much sharper at room temperature in the permanganate titration.

TABLE II

POTENTIOMETRIC TITRATION OF MIXTURES OF FERROUS AND VANADYL SALTS

	1	2	3	4	5	6	7
Ceric used for Fe^{II}, cc	9.03	24.49	24.54	24.50	24.48	9.80	9.75
Ceric calcd. for Fe^{II}, cc	8.99	24 52	24 52	24.52	24.52	9.79	9.79
Ceric used for V^{IV}, cc.........	25.99	29.31	11.66	11.84	11.85	29.72	29.67
Ceric calcd. for V^{IV}, cc.	26.05	29.25	11.70	11 87	11.87	29.71	29.71

The vanadyl chloride solution, **0.05683** *N*, was used in determinations **1–3**, and **0.05735 N** vanadyl sulfate in Nos. **4–7**. The ceric solutions were: **0.05455** N (No. 1), **0.04857** *N* (Nos. 2–3), and **0.04824** N (Nos. **4–7**).

ferro alloys, the method was applied to U. S. Bureau of Standards ferrovanadium No. 61.

A large sample (3.2768 g.) was brought into sulfuric acid solution. (Nitric acid was used and later expelled. The silica was expelled with hydrofluoric acid and the residue was treated with nitric and sulfuric acids.) The solution was made uniform after dilution to 500 cc. Twenty-five cc. portions of the solution were treated in the following ways.

1. The solution was reduced with a slight excess of ferrous sulfate, using the potentiometric method as indicator. Upon titration with standard ceric solution, the distance between the first inflection (room temperature) and the second (50–60°) gave a measure of the vanadium present. Found: **18.40, 18.30, 18.33** cc. of **0.05455** N ceric solution, corresponding to **31.25, 31.08, 31.13%** of vanadium (certificate value, **31.15%** of vanadium).

2. The solutions were oxidized with persulfate in the presence of silver nitrate. The silver was precipitated and the permanganic acid was reduced upon addition of sodium chloride and a little hydrochloric acid. The excess of $K_2S_2O_8$ was decomposed by boiling.[9] The chromic and vanadic acids were determined together by titration with ferrous sulfate that had been freshly standardized against ceric sulfate. The potentiometric method was used. It was not necessary to remove the silver chloride before titration. The vanadium was then determined by titration with ceric sulfate. Found: Cr, **0.56** and **0.53%**; **V, 31.16** and **31.20%**; certificate values; Cr, **0.52**, V, **31.15%**.

Further studies of the direct applications of ceric sulfate in volumetric analysis are in progress in this Laboratory.

Acknowledgment.—The author wishes to make grateful mention of the fact that he completed a portion of the material here presented while working as guest in the chemical laboratory of the Eidgenossische Technische Hochschule, Zürich, Switzerland.

Summary

Dilute vanadyl chloride or sulfate solutions (containing free acid) have been shown to be stable for at least a year.

The potentiometric titration of vanadyl solutions with standard ceric sulfate gives accurate results in simple solutions or in the presence of large quantities of ferric and chromic salts. The vanadyl solution should be heated to 50–60°.

[9] For details see Lundell, Hoffman and Bright, *Ind. Eng. Chem.*, **15,1064 (1923).**

The titration of mixtures of ferrous and vanadyl solutions yields correct results for both iron and vanadium. This process finds practical application in the direct determination of vanadium and the indirect determination of chromium in ferro alloys.

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

THE STRENGTH OF ACETAMIDE AS AN ACID

BY G. E. K. BRANCH AND J. O. CLAYTON

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Introduction

The determination of the strength of a very weak acid, such as acetamide, through measurements of the electrical conductivity of a solution containing both the weak acid and a strong base, necessitates a knowledge of the equivalent conductivity of the resulting salt. This cannot be obtained directly. Consequently measurements must be made under conditions in which the degrees of neutralization of the base differ, and the resulting equations solved for both the equivalent conductivity of the salt and its hydrolysis constant. Such a solution assumes that neither the mobilities of the ions nor the hydrolysis constant of the salt change when the conditions are varied. It is therefore necessary to correct for or avoid changes in these quantities.

Variation in the concentration of total electrolyte will produce marked changes in the mobilities of the ions and in the hydrolysis constant. Consequently our measurements were made at a constant and low value of the concentration of total electrolyte. Since the salt and the base are strong electrolytes of the same valence type, and are both dilute, variation of the ratio between salt and base will lead to negligible errors.

It did not seem possible to correct in any way for the effect of the change of the concentration of acetamide on the hydrolysis constant. This can be avoided by the use of very dilute solutions of the weak acid, but this cannot be done in the case of acetamide, as appreciable reaction between it and a base can only be obtained with concentrated solutions.

The influence of acetamide on the mobilities of the ions cannot be neglected. This difficulty was overcome by the use of an approximate correction formula. The nature and derivation of this formula are discussed later.

Acetamide is so weak an acid that in aqueous solution containing only small concentrations of base its concentration is always very large in comparison with that of its salt. Consequently the presence of very small traces of impurities which either react with a base or are themselves electrolytes will cause an appreciable error in a conductivity measurement. To avoid this difficulty the rates of change of conductivity with change of total base added at constant acetamide concentrations were measured instead of the actual conductivities.

The Method

The method consists of making up a series of solutions containing small but varying quantities of barium hydroxide (0.02 N to 0.08 N) and a constant concentration of acetamide. The conductivities of these solutions were measured at 25° and the results plotted against the concentration of total base added. The slope of this curve at 0.05 N total base is the rate of change of conductivity with variation of total base concentration at the concentration of acetamide which was used. Such a value we have called the L of the solution. Since only small fractions of acetamide, less than 0.01, react with the base, the concentration of free acetamide and the ratio of barium hydroxide to barium acetamide remain constant in any one series of measurements. L is therefore the partial differential of the conductivity with respect to the concentration of total base at a fixed composition of the electrolyte.

Several such values of L at 0.05 N total base were measured at concentrations of acetamide varying between 0 N and 10 N. These values were plotted against the concentration of acetamide (see curve 1 of the figure). From this curve more accurate values of L were obtained at several concentrations of acetamide.

The variation of L with the concentration of acetamide is not only due to differences in the ratios of acetamide ion to hydroxide ion but also to the influence of acetamide on the mobilities of these ions. This latter factor must be corrected for before the ratio base to salt can be obtained.

The equivalent conductivity of an electrolyte at infinite dilution, λ_∞, changes with the nature of the solvent, and this variation may be expressed by the equation $\lambda_\infty \eta =$ a constant, in which η is a property of the solvent only. For solutions of acetamide this may be put in the form $\lambda_\infty/\lambda_{\infty 0} = \eta_0/\eta$, in which the subscript zero indicates that the quantity refers to aqueous solution without any acetamide. This convention will be followed throughout the rest of this article. Now $L = [1-f(N)]\lambda_\infty$, in which $f(N)$[1] is a function of the normality, but is not independent of the nature of the electrolyte. Similarly $L_0 = [1-f_0(N)]\lambda_{\infty 0}$, so that $L/L_0 = (\eta_0/\eta) \times \{[1-f(N)]/[1-f_0(N)]\}$. Now $1-f_0(N)$ must be very nearly equal to $1-f(N)$ when dilute solutions of the same electrolyte at equal concentrations are compared, so that $L/L_0 = \eta_0/\eta = D$, in which D is independent of the nature of the electrolyte. The values of D for various concentrations of acetamide were found by measurements of L

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[1] $f(N)$ is approximately proportional to $N^{1/2}$.

for 0.05 N solution of sodium chloride.[2] It was found that L of sodium chloride is a linear function of the acetamide normality (see curve 2 in the figure). Consequently $L = L_0(1-E[\mathrm{A}])$ in which [A] is the normality of acetamide and E is a property of acetamide related to D by the equation $D = 1-E[\mathrm{A}]$. The corrected values of L were therefore obtained from the equation $L_0 = L/(1-E[\mathrm{A}])$. The value of E was obtained by dividing the slope of L_{NaCl} against [A] by the measured value of $L_{0\mathrm{NaCl}}$.

The L_0 obtained when barium hydroxide is mixed with an acetamide solution is that of a definite mixture of barium hydroxide and barium acetamide. As the base and the salt are both strong electrolytes of the same valence type in dilute solutions, the law of mixtures will be approximately applicable to this property, or $L_0 = \alpha L_{0\mathrm{B}} + (1-\alpha)L_{0\mathrm{S}}$, in which $L_{0\mathrm{B}}$ and $L_{0\mathrm{S}}$ are the values for the pure base and pure salt, respectively, while α is the fraction of the total electrolyte which is the free base. This equation may be more conveniently expressed as $(L_0-L_{0\mathrm{S}})/(L_{0\mathrm{B}}-L_0) = [\mathrm{B}]/[\mathrm{S}]$ in which [B] and [S] are the normalities of the base and salt, respectively. The ratio $[\mathrm{B}]/[\mathrm{S}] = K/[\mathrm{A}]$, in which K is the hydrolysis constant of acetamide ion, so that $(L_0-L_{0\mathrm{S}})/(L_{0\mathrm{B}}-L_0) = K/[\mathrm{A}]$. $L_{0\mathrm{B}}$ was obtained by direct measurement in the absence of acetamide and K and $L_{0\mathrm{S}}$ were obtained by graphical solution from several values of L_0 obtained from the curve. [A] is, of course, always equal to the initial values of acetamide, as never more than 1% of the acetamide was neutralized.

The above method is not applicable to all weak acids and bases. Dissociation constants greater than 10^{-12}, or markedly less than 10^{-15}, cannot be measured in this way. It is also necessary that the acid or base shall be sufficiently soluble; the lower the constant, the greater the solubility necessary.

Results

The experimental results are given below in tabular and graphic form. They were all obtained at 25°.

In Table I the observed values of the specific conductivities in reciprocal ohms per centimeter cube are shown for the various concentrations of acetamide at total barium hydroxide concentrations equal to 0.02 N, 0.04 N, 0.06 N and 0.08 N. The last column shows L, the rate of change of conductivity with change of normality of total base at 0.05 N total base.

The values of L are plotted against the normality of acetamide in curve 1.

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[2] It would have been slightly more accurate to have used $BaCl_2$ instead of NaCl. However the fractional decrease of λ in going from 0 N to 0.1 N is roughly the same for $Ba(OH)_2$ as for NaCl, 0.19 and 0.16, respectively. $f(N)$ is 3/2 of this fraction, so that the slight variation of $\{1-f(N)\}/\{1-f_0(N)\}$ from unity is approximately the same for $Ba(OH)_2$ as for NaCl.

TABLE I

CONDUCTIVITIES OF MIXTURES OF $Ba(OH)_2$ AND CH_3CONH_2 IN AQUEOUS SOLUTION AT 25°

Concn. of CH_3CONH_2, N	Total base = 0.02 N	Total base = 0.04 N	Total base = 0.06 N	Total base = 0.08 N	L at 0.05 N[a]
0	0.00449	0.00863	0.01234	0.01618	0.193
.2	.00428	.00820	.01210	.01561	.189
.4	.00433	.00825	.01220	.01558	.187
.6	.00412	.00777	.01152	.01516	.1835
1.0	.00431	.00766	.01113	.01459	.172[b]
2.0	.00351	.00688	.01001	.01345	.1635
3.0	.00312	.00609	.00898	.01215	.150
6.0	.00227	.00462	.00690	.00921	.116
10.0	.001034	.00270	.00432	....[c]	.0825

[a] The curvature of the plot of conductivity against total base concentration is too slight to be obtained from any series of four measurements; it was assumed that its small variation from a straight line was the same in all cases and equal to that of the plot of the conductivity of barium hydroxide against normality, which can be obtained from the values given in the literature. The best curve of this type was drawn through the four values in each case, and the slope of the line across the curve from 0.02 N to 0.08 N was taken as the value of L at 0.05 N. The uncertainty in choosing the slope was about 0.5%. The values so obtained differ but little from the slopes of the best straight lines drawn through each series of measurements.

[b] This value is not concordant with the other values of L and has been neglected in the determination of the curve of L against the normality of acetamide.

[c] A value of 0.00503 reciprocal ohm was obtained at 0.0682 N total base.

Table II shows the corresponding measurements, using sodium chloride instead of barium hydroxide.

TABLE II

CONDUCTIVITIES OF MIXTURES OF NaCl AND CH_3CONH_2 IN AQUEOUS SOLUTION AT 25°

Normality of acetamide	NaCl = 0.02 N	NaCl = 0.04 N	NaCl = 0.06 N	NaCl = 0.08 N	L at 0.05 N
0	0.00195	0.00372	0.00545	0.00729	0.0879
3	.00202	.00343	.00502	.00654	.0756
6	.00201	.00318	.00453	.00581	.0640
10	.00189	.00283	.00354	....[a]	.0486

[a] A value of 0.00437 reciprocal ohm was obtained at 0.071 N NaCl.

Curve 2 shows the values of L for sodium chloride plotted against the normality of acetamide. It can be seen that the points fall on a straight line within experimental errors. The slope of this straight line is −0.003955, so that E in the equation $L = (1-E[\mathrm{A}])L_0$ is equal to 0.045.

Table III shows in the first two columns values of the normalities of acetamide and the corresponding values of L for 0.05 N barium hydroxide taken from curve 1. The third column shows the corrected values of L, as given by the equation $L_0 = L/(1-0.045[\mathrm{A}])$. The values of the hydrolysis constants are given in the fourth column. These values are calculated from each value of L_0 assuming that the value of L_0 for barium acetamide is 0.0964, which is the value obtained from a solution of the simultaneous equations $(L_0 - L_{0S})/(L_{0B} - L_0) = K/[A]$ the corresponding solution for K is 12.0.

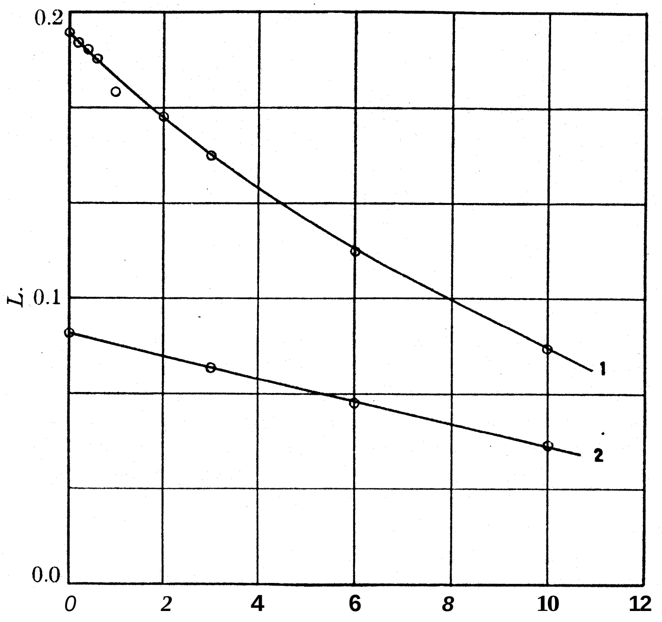

Fig. 1.—Rate of change of conductivity with change of total electrolyte plotted against concentration of acetamide: (1) $Ba(OH)_2$; (2) NaCl.

TABLE III

CORRECTED VALUES OF L AND THE HYDROLYSIS CONSTANT OF ACETAMIDE ION

Normality of acetamide	L	L_0	K (hydrolysis constant of acetamide ion)
0	0.1928	0 1928	. .
0.5	.1847	1801	12 0
1.0	.1771	1855	12 2
2.0	.1631	1792	12 2
3.0	.1502	1736	12 1
4.0	.1382	1686	11 0
5.0	.1272	1641	11 8
7.0	.1075	1569	11 8
10.0	.822	1495	12 3

The close agreement of K does not indicate a corresponding accuracy in the determination, for if there is any trend in the values of K with the normality of acetamide, there would be a corresponding error in the value of L_0 for barium acetamide, such as to make the values of K agree with themselves; so that the hydrolysis constant of acetamide must be taken as equal to 12 ± about 2.

Since the order of L_0 for various electrolytes corresponds roughly to the order of their λ_∞'s, the value obtained for the L_0 of barium acetamide (0.0964) gives us an approximate measure of the mobility of the acetamide ion. This mobility appears to be between that of chloride ion and acetate ion. A mobility very close to that of acetate ion might be expected, so that the value of $K = 12$ is more likely to be too low than too high.

The dissociation constant of acetamide as an acid may be taken as equal to 10^{-14} divided by 12 or 8.3×10^{-16}. The effect of 0.05 N barium salts on the hydrolysis constant has been neglected in obtaining this value, but the error introduced is probably no greater than other uncertainties in the determination. Acetamide is therefore very nearly as strong an acid as it is a base. The basic constant has been measured as 3×10^{-15} at 25° by Walker.[3]

Experimental Details

The usual conductivity apparatus was used. The cell was balanced against a variable box type resistance by means of a Leeds and Northrup Kohlrausch bridge. The two sides were also balanced for capacity by means of a variable condenser. All the measurements at any fixed concentration of acetamide were made at practically the same time, a battery of conductivity cells, previously calibrated against each other, being used. In the time necessary for a comparison of the cells there was no sign of a change of conductivity.

The acetamide was purified by repeated crystallization from ethyl acetate and from chloroform. The characters of the curves obtained by plotting conductivity against concentration of total barium hydroxide added at various acetamide concentrations show that the acetamide was sufficiently pure. Such curves should point toward the ordinate, as the values of L are less than those of λ_∞ at the concentrations used, but if any acidic impurity is present they should point to lower positions on the ordinate, or even appear as if they would cut the abscissa in the more concentrated solutions of acetamide. If the acidic impurity is not all neutralized by the first addition of base, then the curves will tend to flatten out at the lower values of base. The former of these phenomena was observed but the latter was absent. This shows that there was enough acidic impurity (probably ammonium acetate) present to have caused significant errors in conductivity measurements, but not enough to change the values of the rate of change of conductivity with respect to total base added.

Benzamide

An attempt was made to measure the acidic strength of benzamide by the same method. However, only slight changes in the values of L from that of pure barium hydroxide could be obtained with solutions saturated with respect to benzamide. At 0.02 N and 0.04 N benzamide the values of L were about 1 and 2% less than that of pure barium hydroxide. These changes are only about five times as great as those in corresponding solutions of acetamide, so that the rough estimate may be

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[3] Walker, *Z. physik. Chem.*, **4**, **319** (1889).

made that benzamide is about five times as strong as acetamide. Oliveri-Mandala[4] found a value of 1.2×10^{-7} for the acid dissociation constant of benzamide at 20°. If benzamide were so strong an acid, 0.02 N benzamide would have completely neutralized the very dilute solutions of barium hydroxide used, and the values of L should be those of barium benzamide. That this salt has the same L as barium hydroxide is extremely unlikely, so that it may be concluded that the value of 1.2×10^{-7} for the acid dissociation constant of benzamide is erroneous.

Summary

The partial differential of the electrical conductivity of solutions of barium hydroxide with respect to the concentration of total base at constant acetamide concentration was measured at 25°.

The values of this quantity were obtained at several concentrations of acetamide and in pure water. All the measurements were made over the same range of total electrolyte concentration and the differential quantity was estimated in all cases at the same electrolyte concentration.

It has been shown that the influence of acetamide on the mobilities of the ions can be eliminated from these measurements. This correction has been made, and from the variation of the corrected values with the concentration of acetamide, the hydrolysis constant of acetamide ion was calculated. It was found to be 12. This value corresponds to an acid dissociation constant for acetamide equal to 8×10^{-16}.

Similar measurements on benzamide showed that it is an acid whose dissociation constant is between 1×10^{-14} and 1×10^{-15}. A more accurate determination was not possible owing to the low solubility of benzamide in water.

The value obtained for the dissociation constant of benzamide is in marked disagreement with that at present in the literature, which is 1.2×10^{-7} at 20°.

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[4] Oliveri-Mandala, *Gazz. chim. ital.*, 46, I, 298 (1916).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OR MINNESOTA]

VOLUMETRIC DETERMINATION OF FERROUS ION BY MEANS OF POTASSIUM IODATE

BY G. B. HEISIG

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Volumetric solutions of potassium iodate are prepared by dissolving the calculated quantity of pure, dry reagent in water. The solution requires no further standardization, and is permanent. Jamieson[1] reports that a solution of potassium iodate has been kept for ten years without a change of strength. These properties make the reagent particularly valuable to the chemist who makes only an occasional quantitative analysis. Jamieson and others have worked out methods for determining copper, arsenic, antimony, molybdenum, mercury, zinc, tin, hydrazine, hydrogen peroxide, dichromate, tetrathionate, sulfite, thiosulfate and iodide ions. They found that many organic substances did not affect the titrations.

Andrews,[2] in a paper in which he suggests the use of potassium iodate as a volumetric reagent, states that the determination of ferrous ion was unsatisfactory on account of the difficulty of determining the end-point and because iodine was liberated when the solution was allowed to stand. Since no mention is made of the determination of ferrous ion in Jarnieson's book, it seemed worth while to investigate the possibility of a satisfactory method for determining ferrous ion, especially since all the solutions needed were available from other work being done in the writer's laboratory.

A preliminary determination was made at the close of a day and it was found that **10** cc. of a solution of ferrous ammonium sulfate, containing **0.0273** g. of ferrous ion as determined by titration with potassium permanganate, required **9.8** cc. of **0.05** N potassium iodate, corresponding to **0.0274** g. of ferrous ion. The end-point was sharp and permanent.

Later, when experiments were started to work out the details, the results were extremely variable, but all were lower than the calculated values as determined by potassium permanganate titration. The reagents were added in the usual order--concentrated hydrochloric acid, iodine chloride, carbon tetrachloride and potassium iodate—to a solution of ferrous ammonium sulfate containing a little sulfuric acid. Inasmuch as the ferrous ion is known to be much less stable in a hydrochloric acid solution than in a sulfuric acid solution,[3] it occurred to the writer that the difference in results might be accounted for by the partial oxidation of the ferrous ion

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[1] George S. Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., Inc., New York, 1926.

[2] Andrews, Z. anorg. *Chem.*, 36, 83 (1903); THIS JOURNAL, 25, 761 (1903).

[3] Sutton, "Volumetric Analysis," eleventh ed., Blakiston and Sons Co., Philadelphia, Pa., 1924, p. 238.

before the addition of the iodine chloride. If this was the case the iodine chloride should be added before the hydrochloric acid. The ferrous ion would then be oxidized by the iodine chloride rather than by the oxygen in the air. When this change was made in the order of adding iodine chloride and hydrochloric acid, the results checked those obtained with a standard solution of potassium permanganate. The end-point was sharp, and permanent--even after standing overnight.

In order to determine whether or not the increase in the iodine liberated was due to the hydrolysis of the iodine chloride solution before the acid was added, the iodine chloride was mixed with the concentrated hydrochloric acid and the mixture was added to the solution containing the ferrous ion. The results checked those obtained by using potassium permanganate.

To substantiate the theory that the ferrous ion in a concentrated solution of hydrochloric acid was oxidized by the oxygen of the air, carbon dioxide was passed into the flask containing the sample of ferrous ion until the air was displaced. While the stream of carbon dioxide was still passing, concentrated hydrochloric acid was added. The tube through which the carbon dioxide was passing was removed, and the iodine chloride solution and the carbon tetrachloride were added. The amount of ferrous ion which was found was almost the same as that previously determined by titration with potassium permanganate.

To further substantiate this theory, two samples of a solution of ferrous ion, which had been previously standardized with both potassium permanganate and potassium iodate, were placed in similar containers. To one concentrated hydrochloric acid was added, while dilute sulfuric acid (1:5) was added to the other. The containers were covered with filter paper and were allowed to stand for two days with occasional agitation. The sample containing the concentrated hydrochloric acid was titrated with potassium iodate, while the one containing sulfuric acid was titrated with potassium permanganate; 0.65 cc. of 0.1 N potassium iodate was required to titrate the solution containing the hydrochloric acid, whereas 9.83 cc. was required at the beginning of the experiment; 16.3 cc. of 0.0601 N potassium permanganate was required to titrate the solution containing the sulfuric acid; 16.4 cc. was required before exposing to the air.

These results seem to indicate clearly that the ferrous ion must be in a dilute solution of sulfuric acid and not in concentrated hydrochloric acid if the iron is to be maintained in the ferrous condition.

The experimental data showing the effect of changing the order of adding the reagents, etc., are given in Table I.

The procedure finally adopted was to place the sample to be titrated in a glass-stoppered Erlenmeyer flask. Six cc. of the iodine chloride solution and 6 cc. of carbon tetrachloride are added and finally sufficient hydro-

TABLE I

EFFECT OF THE ORDER OF ADDITION OF REAGENTS

Order of adding reagents to the sample		Grams of iron	
First	Second	Taken	Found
HCl	ICl	0.0683	0.0661, 0.0669, 0.0655
ICl	HCl	,0679	.0679
HCl + ICl		,0679	0676
ICl	HCl	0273	.0272, 0 0272
HCl	ICl	0273	.0254, 0 0264
ICl + HCl		0271	0272
CO_2, then HCl	ICl	0554	0550, 0.0550

chloric acid so that the final volume of the mixture contains at least 12% of hydrogen chloride. This corresponds to 50% of concentrated hydrochloric acid by volume. After cooling the mixture, standard potassium iodate solution is added and the contents of the flask are thoroughly agitated after each addition of the reagent. Both $N/10$ and $N/20$ solutions were used in this work. The titration is complete when the violet color of the carbon tetrachloride disappears, showing that the iodine which was liberated has been oxidized to iodine chloride. The end-point is accompanied by a change of the orange color of the aqueous layer to a lemon yellow. If the end-point is exceeded, the excess potassium iodate may be determined by a potassium iodide solution which has been standardized with potassium iodate. The potassium iodate used in this investigation was "Merck's Purified" which had been recrystallized twice from hot water and dried at 120–140° for an hour. Since the iodine in the potassium iodate gains four electrons when it forms iodine chloride, a 0.1 N solution is prepared by dissolving 1/40 of a gram molecular weight in sufficient water to make a liter of solution. The iodine chloride solution was prepared by the method of Jamieson.[4] Ten g. of pure potassium iodide and 6.44 g. of pure potassium iodate were dissolved in 75 cc. of water, and 75 cc. of concd. hydrochloric acid and 5 cc. of carbon tetrachloride were added. If the carbon tetrachloride did not have a faint pink color after shaking vigorously, a potassium iodide solution was added until the presence of a little iodine was noted in the carbon tetrachloride. On the other hand, if the carbon tetrachloride was more than a faint pink, potassium iodate was added to convert some of the iodine into iodine chloride.

The reactions involved in the titration of ferrous iron are

$$2Fe^{++} + 2ICl + HCl \longrightarrow I_2 + 2Fe^{+++} + 2Cl^- + HCl \qquad (1)$$

$$2I_2 + 1KIO_3 + 6HCl \longrightarrow 1KCl + 5ICl + 3H_2O \qquad (2)$$

The solution to be titrated with potassium iodate must contain sufficient hydrochloric acid to prevent the hydrolysis of the iodine chloride which is formed. At least 12% of hydrogen chloride must be present at the end of the titration.

Table II shows the results obtained by these directions.

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[4] Ref. 1, p. 8.

TABLE II

RESULTS ON ANALYSES USING THE STANDARD METHOD

Iron taken, g.	Found, g.	Iron taken, g.	Found, g
0.0557	0.0556	0.0271	0.0272
	.0556		.0271
.1393	.1393	.0679	.0676
	.1391		.0679
.0273	.0272	.0728	.0728
	.0273	.1077	.1077
	.0272		.1075

Ferrous ion can also be determined by adding an excess of potassium iodate to a solution of ferrous ion in dilute sulfuric acid (2 cc. of concd. sulfuric acid per 500 cc. of solution), then adding the hydrochloric acid and carbon tetrachloride and titrating the excess iodate with a solution of potassium iodide whose normality has been determined by titration with potassium iodate. If the hydrochloric acid is added first, and then the excess of potassium iodate, low values for ferrous ion are obtained. The equations for the reactions are

$$4Fe^{++} + 1KIO_3 + 6HCl \longrightarrow 4Fe^{+++} + 1KCl + ICl + 4Cl^- + 3H_2O$$

$$1KIO_3 + 2KI + 6HCl \longrightarrow 3KCl + 3ICl + 3H_2O$$

The results are summarized in Table III.

TABLE III

RESULTS OF ANALYSES USING AN EXCESS OF POTASSIUM IODATE

First	Second	Iron taken, g.	Found, g.
KIO_3 (excess)	HCl	0.0554	0.0553
			.0555
HCl	KIO_3 (excess)	.0554	.0547

In order to determine the effect of organic material, ferrous ion was titrated in the presence of acetic acid, succinic acid, tartaric acid, filter paper, ethyl alcohol and formaldehyde. The procedure adopted was to pipet the sample, which contained 10% of sulfuric acid by volume, into a glass-stoppered flask, add the organic material and about 0.5 g. of pure magnesium to reduce the ferric ion. The mixture was allowed to stand until the magnesium had completely reacted and then the titration was carried out according to the standard iodate method used above. The results obtained are given in Table IV.

TABLE IV

TITRATION IN THE PRESENCE OF ORGANIC MATERIAL

Organic material	Iron taken, g.	Found, g.
Acetic acid, 5 cc.	0.0577	0.0578
Succinic acid, 3 g.	.0577	.0577
Tartaric acid, 3 g.	.0577	.0576
Formalin, 6 cc.	.0577	.0578
Ethyl alcohol, 5 cc.	.0577	.0578
Filter paper	.0577	.0575

The fact that iron can be reduced to the ferrous condition and also titrated in the presence of some organic material greatly increases the usefulness and possibilities of the method.

Summary

1. The ferrous ion is oxidized quantitatively to the ferric ion by iodine chloride and the iodine liberated can be titrated with a standard solution of potassium iodate after adding enough concentrated hydrochloric acid so that the final solution will contain 50% of hydrochloric acid by volume.
2. The ferrous ion can also be determined by adding an excess of standard potassium iodate to a dilute sulfuric acid solution of ferrous ion, and then adding concentrated hydrochloric acid and titrating with a standard potassium iodide solution.
3. The presence of many organic compounds such as acetic acid, succinic acid, tartaric acid, ethyl alcohol, filter paper or formalin does not affect the titration.
4. The method is of especial interest to chemists who are called upon to make occasional analyses, for iodate solutions require no standardization and do not change in strength on keeping.

MINNEAPOLIS, MINNESOTA

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

THE DETERMINATION OF FERROUS IRON IN SILICATE ROCKS. I

BY BYRON A. SOULE

RECEIVED APRIL 21, 1928 PUBLISHED JUNE 5, 1928

The exact determination of ferrous iron in rocks has been conceded to be the most difficult and least satisfactory of all usual determinations in rock analyses.[1]

The Cooke method[2] as modified by Pratt,[3] Barnebey[4] and others, is probably the one most commonly used.

This method involves decomposition of the crushed rock sample by boiling with hydrofluoric and sulfuric acids in a capacious platinum crucible, transfer of the solution to a beaker containing boric acid and titration of the resulting mixture with standardized potassium permanganate.[5]

There are three obvious objections to the method: *(a)* the need for a fairly large (and therefore expensive) platinum crucible, (b) the impossibil-

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[1] (a) Hillebrand, U. S. Geol. Survey, *Bull.*, 700, p. 207; (b) Washington, "The Chemical Analysis of Rocks," John Wiley and Sons, Inc., New York, 3d ed., 1919, p. 183.

[2] Cooke, *Am.* J. *Sci.*, [2] 44, 347 (1867).

[3] Pratt, *ibid.*, [3] 48, 149 (1894).

[4] Barnebey, THIS JOURNAL, 37,1481 (1915).

[5] For details see Washington, ref. lb, pp. 186–191.

ity of seeing when decomposition is complete, and (c) the necessity of transferring the readily oxidized ferrous solution to another dish for titration.

It is, perhaps, not commonly known that a mixture of hydrofluoric and sulfuric acids can be boiled in Pyrex glassware for some time without perforating the container. The same is true in the case of quartz ware which is, in fact, slightly less rapidly dissolved than Pyrex.

Comparative tests of the two materials have demonstrated that quartz is more satisfactory for the permanganate titration of ferrous iron in that it does not appreciably absorb light at the violet end of the spectrum. Even in a vessel of fairly thick, translucent quartz, a permanganate end-point is more readily discerned than in glass. Furthermore, a warning of the approaching end-point is given by an apparent change in the solution from green to colorless just before the true end-point is reached.

In view of these properties and the difficulties mentioned above, it was decided to try both glass and quartz vessels as containers for the decomposition and titration of rock samples. Data presented here cover the work with Pyrex flasks.

Procedure

After many exploratory tests, six new, wide-mouthed, Pyrex, Erlenmeyer flasks of **250** cc. capacity were selected.[6]

The flasks, after cleaning, were weighed, using the heaviest one as a counterpoise. When needed, each flask was filled with carbon dioxide and the sample for analysis introduced. This was immediately followed by **15** cc. of water, **10** cc. of dilute sulfuric acid (1:3) and 5–8 cc. of hydrofluoric acid **(40%).** The flask was next placed on a hot-plate and the liquid gently boiled under a slow stream of carbon dioxide. When, upon swirling the solution, no undecomposed particles were observed, the flask was removed from the hot-plate and a cold, freshly prepared mixture of water **(100 *cc.*),** boric acid (6 g.) and sulfuric acid (**5** cc. of **1**:1) immediately added. After cooling to approximately 15°, which required not over ten minutes, the solution was titrated with standardized potassium permanganate, the amount used being measured in grams.[7] Finally the flask was cleaned and weighed.[8]

Results

In order to determine whether anything that had gone into solution during the dissolving process would reduce permanganate, blanks were

TABLE I

BLANK DETERMINATIONS

Flask no.	Time, min.	Temp., °C.	Glass diss., g.	$KMnO_4$, g. soln.	$\frac{\text{G. }KMnO_4}{\text{G glass}}$
2	25	98	1.091	2.335	2.140
4	20	98	1.020	2.173	2.130
				Av.	2.135

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[6] While an effort was made to secure samples from different lots, there is no assurance that this objective was attained.

[7] The volume of solution at the end was about 150 cc. for the majority of samples.

[8] The average flask life in this work was found to be about twenty determinations.

run, omitting only the ferrous material. Some of the results are given in Table I, which also includes the duration and approximate temperature of reaction.

A consideration of the analysis of Pyrex glass by Walker and Smither[9] would indicate only two sources of reducing action. Some of the iron or arsenic or both might be in the lower valence rather than the higher, as there reported, since arsenic is commonly added, when making glass, in the form of As_2O_3 to reduce any ferric iron present as an impurity in the raw materials. In any case the figures obtained when dividing the weight of glass dissolved by the weight of permanganate consumed apparently cannot be used as a correction factor in an actual analysis (see Table III, col. 5).

The only satisfactory way thus far found to determine the factor is to run a series of determinations using a compound of known ferrous iron content. Under these conditions the excess permanganate consumed, divided by the weight of glass dissolved, does give a dependable factor. This factor can obviously be applied in calculations involving other normalities of permanganate. Data for the correction factor obtained are given in Table II, the standard ferrous ammonium sulfate containing 18.27% of iron as FeO.

TABLE II

DATA USED IN DETERMINATION OF CORRECTION FACTOR

Normality of $KMnO_4$ = 0.04803; $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ = 18.27% FeO; time of boiling = 25 minutes

Sample,	Glass diss., g	Excess $KMnO_4$, g. soln	G. excess $KMnO_4$ / G. glass
0.4070	1.316	1.651	1.255
.4079	1.395	1.739	1.247
.4512	1.280	1.599	1.249
		Av.	1.250

Using the figures 1.250 as a basis for correcting the original data given in Table III, the results in the last column were secured.

TABLE III

ANALYSIS OF MAGNETITE (7) FOR FERROUS IRON. APPLICATION OR CORRECTIONS FOR REDUCTION DUE TO MATERIAL IN GLASS DISSOLVED

Normality of $KMnO_4$ = 0.04972

Sample g.	Time, min.	Glass dissolved, g.	FeO, %		
			Uncorr.	C.F.—2.135	C.F.—1.250[a]
0.3048	25	1.093	41.47	38.74	39.82
.3035	20	0.918	41.16	38.85	39.76
.3763	20	.972	41.08	39.11	39.89

[a] The correction, considering difference in normality = (0.04972 × 1.250)/0.04803.

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[9] U. S. Bureau of Standards, *Tech. **Paper*** 107, **p.** 8. The figures given are

Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	SiO_2	B_2O_3	As_2O_5
2.0	0.25	0.01	0.29	0.06	4.4	0.20	80.5	11.8	0.70

Notes

1. This material when received was labeled "Magnetite." Obviously the FeO content is almost 9% too high for a true magnetite. It is expected that a complete analysis with mineralogical and geological data will be published elsewhere.

2. Samples for the above analyses were portions of a single crystal, crushed to a coarse powder, about twenty mesh.

In Table IV are given results for a variety of silicate rocks. All samples were crushed to forty mesh and finer.

TABLE IV

ANALYSIS OF SILICATES FOR FERROUS IRON

Normality of $KMnO_4$ = 0.04803

Sample	Weight, g.	Time, min.	Glass diss., g.	$KMnO_4$ (corr.), g. soln.	FeO, %
1	0.5376	12	0.692	2.967	1.90
	.5340	12	.851	2.871	1.85
2	.3083	17	.912	3.843	4.30
	.4995	19	1.463	6.291	4.35
3	.4779	8	0.374	10.981	7.93
	.4428	8	.486	10.243	7.98
	.5433	8	.447	12.476	7.92
4	.4435	8	.419	10.805	8.41
	.5473	7	.390	13.272	8.37
	.4872	8	.405	11.826	8.38
5	.5090	20	1.449	15.170	10.28
	.5846	21	0.873	17.313	10.22
	.6600	20	1.139	19.584	10.24

No. 1—Andesite, Arakebesan Island; No. 2—Andesite, Bonin Island; No. 3—Basalt, Arizona; No. 4—Basal Basaltic Glass, Arizona; No. 5—Basalt (Ponape), Tolatik Island.

Summary

1. Platinum ware is not absolutely essential for the determination of ferrous iron in rocks.

2. Silicate samples can be dissolved by boiling with hydrofluoric and sulfuric acids in Pyrex flasks and, subject to the usual interferences, the solution obtained may be titrated for ferrous iron.

3. A glass container has two marked advantages over one of platinum: *(a)* the completeness of decomposition may be readily observed, and (b) transfer of the solution from one dish to another for titration is unnecessary.

4. A correction factor for Pyrex glass has been determined.

ANN ARBOR, MICHIGAN

NOTE

Note on the Purification of Potassium Dihydrogen Phosphate.—It is a matter of common observation in chemical laboratories that many solutions deposit sediments on standing in glass bottles for any length of time. Besides being unsightly this phenomenon causes the worker to doubt the purity of his reagents and the actual concentration of the solutions. The fifth molar solution of potassium dihydrogen phosphate used in preparing Clark and Lubs' standard buffer solutions is usually seen to deposit a sediment on the bottom of the stock bottle. Because of the fact that it is of prime importance that the reagents used in the preparation of regulatory buffer mixtures be of exceptional purity and constant composition, some work has been done in this Laboratory to determine the nature of the sediment and factors influencing its deposition.

It has been found that the material of the container has no effect; soft and hard glass, paraffin and silver were used, and all give equal amounts of sediment when an equal amount of solution is placed in each. The deposition is found to be more rapid at higher temperatures and more complete the less the concentration of salt in the solution. At a temperature of about 85° (on a water-bath) the sediment is thrown out completely in about twenty-four hours, while at room temperature the time taken is considerably longer. If the concentration of salt is greater than 0.2 M the sediment is found to stay in suspension. Even if three times recrystallized the salt always contains some impurity, for the sediment forming impurity is soluble in hot saturated KH_2PO_4 solutions and cannot be removed completely by filtration.

On analysis, the sediment from a 0.2 M solution of a "specially purified and standardized" commercial salt has been found to be largely a mixture of colloidally aggregated aluminum and ferric compounds. The occurrence of aluminum as an impurity was first pointed out to us by the La Motte Chemical Products Company.[1] Sediments from solutions of salts obtained from other sources contained alkaline earth metals in addition. No silicon has been found present in any of the sediments. It is interesting to note that no alkali phosphate salt containing an ammonium ion, for example, sodium diammonium phosphate, $Na(NH_4)_2PO_4$, gives a sediment from solution. During the commercial preparation of the salts, the iron and aluminum impurities of the phosphoric acid have probably been thrown out as phosphates. However, one commercial sample of potassium dihydrogen phosphate, of "c. p." quality, was found to be free from any sediment producing impurity. In all, salts from four different sources were examined.

For the purification of a potassium dihydrogen phosphate salt which may

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[1] McCrumb, private communication, January, 1928.

contain the impurities mentioned above, the following procedure is recommended. Make up an approximately fifth molar solution of the salt, let it stand in a flask, sealed to prevent excessive loss of water, for twenty-four hours on a water-bath at 75–55". Then filter through a very retentive paper or asbestos filter and recrystallize by the usual methods the residue left on evaporation. By this means a salt of higher purity can be obtained in one recrystallization than can be obtained by the three recrystallizations from water recommended by Clark.[2] In place of evaporation to complete dryness, the salt may be precipitated from a cold saturated solution (obtained by partially evaporating and cooling the filtered solution) to which is added an equal amount of cold 95% ethyl alcohol. This gives very small crystals which may be used as such or which may be further recrystallized from water.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

CATALYTIC OXIDATION OF FURFURAL IN THE VAPOR PHASE

BY WILLIAM V. SESSIONS

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Introduction

During the course of recent investigations upon the catalytic oxidation of furfural in aqueous solutions,' it was found that by use of various metallic oxide catalysts, different products could be obtained. Among these products were fumaric acid, mesotartaric acid and oxalic acid. The purpose of the present investigation was to determine what products are formed when furfural is oxidized in the vapor state with a similar catalyst.

Experimental Part

To prepare the catalyst, vanadic acid was precipitated upon asbestos by adding hydrochloric acid to a solution of ammonium vanadate, the asbestos filtered, washed, dried and ignited to free it from ammonium chloride and to convert the vanadic acid into vanadium pentoxide.

The catalytic mass showed a tendency to become less active during the course of the experiments, undoubtedly due to some form of poisoning. For regeneration, it was necessary only to redissolve the vanadium pentoxide in ammonia and reprecipitate with hydrochloric acid

The furfural used in these experiments was the ordinary commercial article, which is dark colored and contains about 1% of water. It was employed without redistillation.

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[2] Clark, "The Determination of Hydrogen Ions," 2nd ed., Williams and Wilkins, Baltimore, Md., 1922, p. 100.

[1] Milas, THIS JOURNAL, 49, 2005 (1927).

The furfural was placed in a 300cc distilling flask to which was fitted a right angled tube with a flare at the end projecting into the liquid. This served to break up the air current. A soda lime drying tube was connected to the other end to absorb any atmospheric carbon dioxide. The flask rested in a water-bath which could be maintained at an even temperature by an electric hot-plate The side arm of the distilling flask extended into a Pyrex catalysis tube through a two-holed cork stopper, a 500° thermometer projecting through the other hole and extending into the middle of the asbestos. This served to indicate the temperature of the contact mass. The catalysis tube was heated by an electric furnace whose temperature was controlled by variable resistances. To the tube was fitted a long Pyrex adapter for the condensation of the oxidation products. An additional receiver was furnished by a water cooled flask. In series with this flask was a spiral condenser to condense any possible low boiling products. To the top of the condenser was fitted a gas washing bottle containing a solution of sodium hydroxide free from carbonate. A stream of air was drawn through the whole apparatus by means of a water pump attached to the bottle.

The velocity of the vapors through the system could be controlled by means of the water pump and the ratio of furfural to oxygen in the vapors by varying the temperature of the water-bath around the flask containing the furfural. For each run, the loss in weight of this flask was taken as the weight of furfural sent through the reaction tube. Conditions of temperature were varied in the several runs in order to find those necessary for the best yield.

Unchanged furfural was identified in the end products by its color reactions with resorcinol or phloroglucinol and sometimes by its boiling point and odor. Formaldehyde was identified by its odor and color reaction with resorcinol, wherein it differs from furfural. Water was sometimes present in sufficient quantity for identification by its boiling point; otherwise the blue color imparted to anhydrous copper sulfate showed its presence. Carbon dioxide was always to be found in the alkaline solution in the wash bottle. Maleic anhydride formed in the receivers as long white needles melting at 53°. Maleic acid was also present as clear, prismatic crystals melting at 138.5–140° (corrected). On recrystallization from water, the crystals melted at 138–139° (corrected). When recrystallized from an alcohol–benzene mixture, the melting point decreased with successive crystallizations until it became constant at 130–131°, which is the temperature generally given in the literature. The product was further identified as maleic acid by titration with tenth normal sodium hydroxide and also by carbon and hydrogen analysis, showing 3.57% H and 41.08% C against a calculated percentage of 3.47% H and 41.38% C.

A number of runs were made under various conditions of temperature, time and rate of flow of the air–furfural vapors over the catalyst. The best conditions seemed to be to keep the catalyst at temperatures from 200–300° and the furfural at a temperature of 45–50' while the air was passing through it. This represents a concentration of approximately one part of furfural to twelve of oxygen. Too rich a mixture gives unoxidized furfural in the product. In any case the yields were very poor, the best being 5.5 g. of maleic acid from 38 g. of furfural. Too low a temperature of the catalyst results in little or no oxidation; too high a temperature yields only carbon dioxide and water. The latter also is true when oxygen is used instead of air. Removing the product from the catalyst at a more rapid rate, obtained by increasing the rate of vapor flow, effected no marked increase in yield.

As to the mechanism of the reaction which takes place, it seems probable that at the temperature of the catalyst, maleic anhydride is formed according to the equation

$$C_4H_3OCHO + 2O_2 \longrightarrow C_4H_2O_3 + CO_2 + H_2O$$

but as maleic anhydride is readily converted to the acid in the presence of water, and water is one of the oxidation products, maleic acid is also found in the receivers. No fumaric acid could be isolated either from the end-products or the mother liquors. The formaldehyde is assumed to be a product of the further oxidation of the maleic anhydride, as whenever maleic acid was found in the receivers, formaldehyde as well as carbon dioxide and water could be identified.

It was observed that a solid phase separated in the distilling flask containing the furfural after air had been drawn through for some time. This material was somewhat rubbery in nature, but when dried and the occluded furfural removed with alcohol, it proved to be a rather granular solid, dark brown in color and quite insoluble in organic and inorganic reagents. It had no apparent melting point, merely charring.

Conclusion

When furfural is oxidized with air at temperatures from 200–300° in the presence of vanadium pentoxide as a catalyst, small amounts of maleic acid and maleic anhydride are formed, as well as formaldehyde, carbon dioxide and water.

The maleic acid formed is evidently quite pure and has a melting point of 138.5–140°.[2]

PRINCETON, NEW JERSEY

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[2] This value has been observed by Rinckes, *Rec. trav. chim.*, 45, 822 (1926), and in 1922 Dr. H. T. Clarke of the Eastman Kodak Co. prepared some melting at 142–143°.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

SODIUM SALTS OF AROMATIC NITRILES. I[1]

BY MARY M. RISING AND TSOH-WU ZEE[2]

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While investigating methods of drug synthesis the authors have discovered a series of sodium salts of aromatic nitriles, intermediates in the production of certain medicinals. As so often happens in research, the incidental discovery has proved to be of more consequence than are the findings from all the rest of the investigation; these nitrile derivatives are of peculiar importance from the theoretical aspect, and of considerable value as preparative agents.

An earlier paper[3] describes the preparation of α-sodium-α-phenylbutyronitrile, a member of the new series, and discusses the properties of the salt. This work was made the point of departure for a systematic investigation of other salts of the same type and the present paper describes the synthesis and behavior of sodiumphenylacetonitrile, which, like α-sodium-α-phenylbutyronitrile, apparently exists in tautomeric nitride and carbide forms, of structures $(C_6H_5)HC{=}C{=}NNa$ and $(C_6H_5)(CN)HCNa$, respectively. The earlier discussion of a-sodium-a-phenylbutyronitrile is amplified and the importance of both salts from the point of view of organic theory is emphasized.

Metal derivatives of nitriles have been studied by a number of chemists. Victor Meyer[4] recognized the salt-forming property of phenylacetonitrile and similar nitriles and believed their salts to be carbides. Thus he would assign to sodium phenylacetonitrile the structure $(C_6H_5)(CN)HCNa$.

Ernst von Meyer[5] and his students[6] made an extended study of sodium

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[1] The contents of this article were reported upon at the Midwest Regional Meeting of the American Chemical Society in May, 1927, at Chicago.

[2] This paper describes work done by Tsoh-Wu Zee in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago. 1926. The experimental work was done by Dr. Zee. Since he left for China the effort has been made in the Kent Laboratory to repeat his work. Up to the present time we have been unable to obtain the salts in pure form. The evidence that Dr. Zee actually obtained them is entirely convincing: (1) sodiumphenylacetonitrile was converted into α-phenyl butyronitrile by treatment with ethyl iodide. (2) α-Sodium-α-phenylbutyronitrile was converted into phenylethylmalonic dimethyl ester by treatment with chloroformic ester and conversion of the cyano-ester so obtained into the malonic ester. These reactions and other internal evidence that the salts were obtained are fully described in this paper and the one referred to in Ref. 3. Moreover, recent re-analyses of Dr. Zee's salts show them to be pure compounds of the composition previously assigned to them on the basis of quantitative analyses. We are making every effort at the present time to obtain the salts by the Zee method, and by other methods.

[3] Rising and Zee, THIS JOURNAL, 49, 541 (1927).

[4] Victor Meyer, Ber., 21, 1291 (1888).

[5] E. von Meyer, J. *prakt.* Chem., 22, 262 (1880); 38, 336 (1895); 52, 81 (1895).

[6] Holtzwart, *ibid.*, 38, 343 (1889); 39, 230 (1889); Wache, *ibid.*, 39, 245 (1889).

derivatives of aliphatic nitriles and of phenylacetonitrile. This work will be discussed later in connection and comparison with our own.

Nef and some of his students, notably Hesse, have contributed largely to our knowledge of the behavior and structures of the salts of nitriles and related compounds. Nef was particularly interested in the constitution of the salts, and considered that the metal atom is held by nitrogen, just as in salts of hydrocyanic acid, the latter being the parent substance of nitriles.[7] Hesse[8] studied the sodium salt of cyanoacetonitrile. He found that the compound evolves hydrocyanic acid upon treatment with strong acid and concluded that the metal in the salt is attached to nitrogen; his structure for the salt is that of a nitride, $(CN)HC{=}C{=}NNa$.

The behavior of sodiumcyano-acetonitrile bears a striking resemblance to that of the salts of aromatic nitriles prepared by us. Phenylacetonitrile and a-phenylbutyronitrile are salt forming by virtue of the hydrogen atom carried by the carbon atom adjacent to the nitrile group. By their separate treatment with sodium globules in dry ether at room temperature there are produced in excellent yields the solid salts sodiumphenylacetonitrile and a-sodium-a-phenylbutyronitrile. Equations for these reactions follow.

$$2(C_6H_5)CH_2(CN) + 2Na \longrightarrow 2(C_6H_5)HC{=}C{=}NNa + H_2\uparrow \tag{1}$$

$$2(C_6H_5)(C_2H_5)HC(CN) + 2Na \longrightarrow 2(C_6H_5)(C_2H_5)C{=}C{=}NNa + H_2\uparrow \tag{2}$$

The salts show two well defined and significant sets of properties which throw light upon their constitution: (1) they are decomposed by water and all acids; (2) they react by substitution.

Behavior of Sodium Salts with Acids. **Sodiumphenylacetonitrile.**—Treatment of this salt with cold sulfuric acid caused an evolution of hydrocyanic acid and the formation of an oil of boiling point 204–205" which proved to be benzyl alcohol. The hydrocyanic acid formed in the reaction was identified by qualitative test and determined quantitatively. The benzyl alcohol was identified in two ways: (1) by oxidation to benzaldehyde and conversion of the aldehyde into benzaldehydephenylhydrazone; (2) by conversion into 3-nitrophthalic a-monobenzyl ester.[9]

α-Sodium-α-phenylbutyronitrile.—When this salt was treated with cold sulfuric acid evolution of hydrocyanic acid occurred and a yellow solid of melting point 89–90° was formed which proved to be symmetrical diethylstilbene, $(C_6H_5)(C_2H_5)C{=}C(C_2H_5)(C_6H_5)$. The hydrocyanic acid was identified by qualitative test and measured quantitatively. The solid product of melting point 89–90" was shown to be diethylstilbene (I) by analysis and (2) by conversion into the dibromide $[(C_6H_5)(C_2H_5)CBr]_2$.

The reactions of the salts with acid are believed to occur in successive stages

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[7] Nef, *Ann.*, **287**, 265 (1895).

[8] Hesse, Doctor's *Dissertation*, University of Chicago, 1896.

[9] Nicolet and Sacks, THIS JOURNAL, **47**, 2348 (1925).

$$(C_6H_5)HC{=}C{=}NNa + H_2SO_4 \longrightarrow (C_6H_5)HC{=}C{=}NH + NaHSO_4 \tag{3}$$

$$(C_6H_5)HC{=}C{=}NH \longrightarrow HN{=}C{=}\uparrow + (C_6H_5)HC{=} \tag{4}$$

$$(C_6H_5)HC{=} + HOH \longrightarrow (C_6H_5)H_2COH \tag{5}$$

and

$$(C_6H_5)(C_2H_5)C{=}C{=}NNa + H_2SO_4 \longrightarrow (C_6H_5)(C_2H_5)C{=}C{=}NH + NaHSO_4 \tag{6}$$

$$(C_6H_5)(C_2H_5)C{=}C{=}NH \longrightarrow HN{=}C{=}\uparrow + (C_6H_5)(C_2H_5)C{=} \tag{7}$$

$$(C_6H_5)(C_2H_5)C{=}+{=}C(C_2H_5)(C_6H_5) \longrightarrow (C_6H_5)(C_2H_5)C{=}C(C_2H_5)(C_6H_5) \tag{8}$$

Certain features of these reactions are worthy of emphasis. (1) The sodium salts are assigned the structures of nitrides; the presence of the group $—C{=}C{=}NNa$ accounts for the formation of hydrocyanic acid. (2) The weak and unstable acids $(C_6H_5)HC{=}C{=}NH$ and $(C_6H_5)(C_2H_5)C{=}C{=}NH$ are thought to decompose spontaneously into hydrocyanic acid and the unstable fragments $(C_6H_5)HC{=}$ and $(C_6H_5)(C_2H_5)C{=}$, respectively. (3) The absorption of water by the bivalent carbon atom of the fragment $(C_6H_5)HC{=}$ explains the formation of benzyl alcohol from sodium phenylacetonitrile; two of the similarly unsaturated fragments $(C_6H_5(C_2H_5)C{=}$ from a-sodium-a-phenylbutyronitrile may unite to form diethylstilbene.

The decomposition of a-sodium-a-phenylbutyronitrile with acid was found to furnish the amount of hydrocyanic acid demanded by our theory, but only 69% of the expected amount of diethylstilbene (equations 6–8). The similar decomposition of sodiumphenylacetonitrile produced only 49% of the amount of hydrocyanic acid and 52% of the benzyl alcohol demanded by equations 3-5. Two questions at once arise. Why should not both the salts be decomposed quantitatively into hydrocyanic acid? No data at present available afford an answer to this query. Further, why should not the treatment of sodiumphenylacetonitrile with acid produce the olefin, symmetrical diphenylethylene, $(C_6H_5)HC{=}CH(C_6H_5)$, in addition to benzyl alcohol, and why should not a-phenylpropyl alcohol, $(C_6H_5)(C_2H_5)HCOH$, be formed from a-sodium-a-phenylbutyronitrile and acid, in addition to diethylstilbene? The failure to isolate diphenylethylene and α-phenylpropyl alcohol does not preclude entirely the possibility of their formation, which would account for the low yields of benzyl alcohol and diethylstilbene obtained. Further efforts will be made to determine the fate of that part of the salts so far unaccounted for in their reaction with acid.

Substitution Reactions of Sodium Salts.—An entirely different type of reaction is shown by a-sodium-a-phenylbutyronitrile when the salt is treated with an alkyl iodide or chloroformic ester: here substitution occurs, the alkyl or carbalkoxy group becoming attached to the carbon atom carrying the phenyl group in the nitrile. For instance, with chloroformic methyl ester in dry ether the salt reacts to form a-phenyl-a-cyanobutyric methyl ester, $(C_6H_5)(C_2H_5)C(CN)(CO_2CH_3)$. The identity of the cyano ester was definitely established by its conversion into phenylethylmalonic dimethyl ester, $(C_6H_5)(C_2H_5)C(CO_2CH_3)_2$, in a series of reactions described in a previous report.[10] The fact that the substituting group attaches itself to a carbon atom rather than to nitrogen is evidence in favor of a carbide structure for the salt taking part in substitution reactions, $(C_6H_5)(C_2H_5)(CN)CNa$. In a similar way, the alkylation of sodiumphenylacetonitrile leads to the production of a-phenylbutyronitrile, and the structure of the salt so reacting is considered to be that of a carbide, $(C_6H_5)(CN)HCNa$.

The "double behavior" of our sodium salts has convinced us that each exists in two forms, a nitride, which produces hydrocyanic acid when treated with acid, and a carbide, which is reactive in substitutions; and that the nitride and carbide are tautomers. The situation is probably more accurately expressed in an assumption of tautomerism of the negative ions of the salts. For example, the nitride and carbide forms of sodiumphenylacetonitrile are ionized

$$[(C_6H_5)HC{=}C{=}N]Na \rightleftharpoons [(C_6H_5)HC{=}C{=}N^-] + Na^+ \tag{9}$$

and

$$[(C_6H_5)(CN)HC]Na \rightleftharpoons [(C_6H_5)(CN)HC^-] + Na^+ \tag{10}$$

The nitride and carbide ions are mutually convertible

$$[(C_6H_5)HC{=}C{=}N^-] \leftrightarrows [(C_6H_5)(CN)HC^-] \tag{11}$$

An analogous tautomeric relationship of the nitride and carbide ions of a-sodium-a-phenylbutyronitrile is probable. The use of a substituting agent would force the tautomerization expressed in Equation 11 to the right; this change could be reversed by treatment of the carbide salt with acid.

An obvious corollary to the tautomeric relationship of the nitride and carbide salts is the existence of tautomeric forms of phenylacetonitrile and a-phenylbutyronitrile

$$(C_6H_5)H_2C(CN) \rightleftarrows (C_6H_5)HC{=}C{=}NH \tag{12}$$

$$(C_6H_5)(C_2H_5)HC(CN) \rightleftarrows (C_6H_5)(C_2H_5)C{=}C{=}NH \tag{13}$$

The two forms of each nitrile may be designated as "nitrile" and "imide;" the relationship of nitrile and imide to the carbide and nitride salts, respectively, should be apparent. The accomplishment of the separation of the tautomeric forms of the nitriles would constitute valuable evidence for the theory of tautomerism. The attempt to perform this separation in the case of a-phenylbutyronitrile is already under way and interesting results have been obtained which will be reported when the investigation has been completed.

The assumption of tautomerism offers a simple explanation of the behavior of the salts discussed and of the nitriles themselves. Apparently

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[10] **Ref.** 3, p. 544.

their treatment with sodium produces nitrides, the metal reacting with the trace of "imide" nitrile present. When the nitrides are treated with acid no tautomerization occurs since it is the nitride form which reacts to form hydrocyanic acid. When, however, the nitride salts are in suspension in dry ether in the presence of a substituting agent such as chloroformic ester, the salts, being measurably soluble in ether, are dissociated slightly and an opportunity for tautomerization of the nitride into the carbide ion would be afforded. As the latter is used up in the substitution reaction, tautomerization proceeds until all of the nitride ion is converted into carbide.

The work so far described thus inaugurates an intensive study of nitride-carbide tautomerism of certain nitriles and their salts. There are a number of points of similarity between this type of tautomerism and the enol-keto variety of acetoacetic ester.

The sodium salts discussed are theoretically interesting from quite another point of view, which will be most clearly understood from a consideration of the work of E. von Meyer.[5] He studied the reaction of aliphatic nitriles and of phenylacetonitrile with sodium in dry ether at the boiling point of ether. Von Meyer summarizes the reaction of the latter nitrile with sodium as follows

$$3C_6H_5CH_2CN + 2Na \longrightarrow NaCN\ 4\ C_6H_5CH_3 + C_{16}H_{13}N_2Na \qquad (14)$$

The salt $C_{16}H_{13}N_2Na$ yielded on treatment with acid an oil of composition $C_{16}H_{14}N_2$. Von Meyer proved its structure to be $C_6H_5CH_2C({=}NH)$-$CH(C_6H_5)(CN)$.

It is desired to emphasize two features of von Meyer's work in relation to our own. The first of these is the more important and concerns the essential nature of the reactions under consideration. In his attempt to devise a mechanism for the reaction of nitriles with sodium, von Meyer assumed the formation of intermediate compounds; for example, the salt sodiumacetonitrile, CH_2NaCN, from acetonitrile and sodium. He did not, however, isolate any such intermediate. This salt was considered to react with acetonitrile to form a sodium salt of dimolecular acetonitrile, $C_4H_5N_2Na$. Reasoning similarly for phenylacetonitrile, the salt C_6H_5-$CHNaCN$ was assumed to be formed, though not isolated. This substance is none other than the sodiumphenylacetonitrile which we have obtained in pure form. The reaction of sodiumacetonitrile with acetonitrile, or of sodiumphenylacetonitrile with phenylacetonitrile, to form salts of dimolecular nitriles resembles very closely an aldol condensation, the condensation products being $CH_3C({=}NNa)CH_2CN$, and $C_6H_5CH_2C({=}NNa)$-$CH(C_6H_5)(CN)$, respectively. The formation of such intermediate compounds as CH_2NaCN and $C_6H_5CHNaCN$ is demanded by the modern theory of aldol condensations, but their isolation occurs very rarely, doubtless on account of their extreme instability. It would appear that we have succeeded in isolating two such intermediate products. Confirmatory evidence of our hypothesis will be sought in an attempt to produce sodium dimolecular phenylacetonitrile, $C_6H_5CH_2C({=}NNa)CH(C_6H_5)(CN)$, by condensation of sodiumphenylacetonitrile with phenylacetonitrile.

The second point of contact between von Meyer's work and our own concerns the variation in products obtained by him and by us. In our work there was no indication of the formation of a sodium salt of a dimolecular nitrile, nor of sodium cyanide, nor of a paraffin, from the nitriles and sodium under the conditions used. That our products were pure monomolecular sodium salts and that there was no indication of the formation of sodium salts of dimolecular nitriles, or of sodium cyanide, has been proved conclusively from the analytical data, a typical set of which follows.

TABLE I

PERCENTAGE COMPOSITION OF SODIUMPHENYLACETONITRILE AND RELATED COMPOUNDS

	Composition of sodiumphenyl-acetonitrile, NaC_8H_6N		Composition calcd. for reaction product containing 1 part sodium cyanide to 1 part dimolecular sodium salt (Eq. 14), %	Composition of dimolecular sodium salt, $NaC_{16}H_{13}N_2$, %
	Calcd., %	Found, %		
Na	16.53	16.23	15.07	8 97
N	10.07	10.32	13.77	10.93
C	69.03	69.28	66.85	74.96
H	4.34	4.58	4.29	5.11

These figures show that our salt is pure sodium phenylacetonitrile. The analytical data for α-sodium-α-phenylbutyronitrile are to be found in the Experimental Part of this paper and constitute ample evidence of its purity.

A vital question presents itself as to the cause of the differences in results obtained by von Meyer and by ourselves. It has seemed to us to be important to make a thorough study of this phase of the problem and experimental work in progress at the present time should enable us to formulate a definite answer to the question, which will appear in a later report.

The work so far described is but the beginning of a series of more extensive investigations. Among the most important and interesting of these are the following: (1) the effort to separate the tautomeric forms of α-phenylbutyronitrile will be continued. (2) Silver salts of the nitriles will be prepared if possible, and alkylated. They should yield N-alkyl derivatives of the type $(C_6H_5)HC{=}C{=}NR$. (3) The attempt will be made to obtain the sodium salt of a dimolecular nitrile by condensation of sodiumphenylacetonitrile with phenylacetonitrile. (4) We shall try to improve the low yields obtained in the alkylation of the two sodium salts discussed. (5) Further knowledge of the behavior of salts of nitriles will be sought in a study of analogous salts.

Experimental Part

1. **Sodiumphenylacetonitrile, $(C_6H_5)HC{=}C{=}NNa$ or $(C_6H_5)(CN)HCNa$.**—The procedure followed for the preparation of sodiumphenylacetonitrile was the same as

that used to obtain its homolog, α-sodium-α-phenylbutyronitrile.[11] The product of the reaction, a yellow amorphous solid, was shown by analysis to be pure sodiumphenylacetonitrile.

Anal. Subs., 0.4420, 0.0822: Na_2SO_4, 0.2216, 0.0414. Calcd. for NaC_8H_6N: Na, 16.53. Found: 16.23, 16.30. Subs., 0.1852, 0 2732: N_2, 17.05 cc. (20°, 743.5 mm.), 25.38 cc. (22°, 745 8 mm) (over 50% KOH). Calcd. for NaC_8H_6N: N. 10.07. Found: 10.32, 10.34. Subs., 0.2385. 0.1959; CO_2, 0.6059, 0.4984; H_2O, 0.0983, 0.0806. Calcd. for NaC_8H_6N: C. 69.03; H, 4.34. Found: C, 69.28, 69.38; H, 4.58, 4.57.

Yields of the salt were good, between 80 and 90%. Equations expressing this reaction and others to be discussed subsequently are to be found in the theoretical discussion.

Behavior with Acid. (1) Determination of Hydrocyanic Acid.—Sodiumphenylacetonitrile is decomposed by acids with liberation of a gas and formation of a yellow oil. The gas was shown by qualitative test to be hydrocyanic acid and was determined quantitatively. For this purpose sodiumphenylacetonitrile (10 g.) was placed in a flask fitted with a two-holed stopper which carried a dropping funnel and an outlet tube, the latter leading into dilute sodium hydroxide (50 cc.) contained in a side arm flask. Fifty per cent. sulfuric acid[12] was dropped slowly upon the salt from the dropping funnel, whereupon there occurred a brisk evolution of hydrocyanic acid which lasted some moments. The gas was brought into the alkali by means of suction, air entering the system through the dropping funnel. After this operation was finished the alkali was neutralized with dilute sulfuric acid and the cyanide present in it was determined by titration with silver nitrate, potassium iodide being used as indicator.[13]

Anal. Subs., 10.2000, 5.1738: 36.10, 18.25 cc. of *N* $AgNO_3$, factor 0.9960. Calcd. for NaC_8H_6N: CN, 18.70. Found: 9.16, 9.13.

Thus about 49% of the amount of hydrocyanic acid demanded by Equation 4 was produced.

(2) Separation and Identification of Benzyl Alcohol.—The sulfuric acid solution remaining from the decomposition of sodiumphenylacetonitrile just discussed was extracted twice with ether to remove the oil produced by treatment of the salt with acid. The ether extracts were washed twice with sodium carbonate and dried over anhydrous sodium sulfate. Fractionation of the oil remaining after the removal of the ether yielded 4 g. of distillate of boiling point 204–205°; pure benzyl alcohol boils at this temperature. A tarry residue remained in the distilling flask. The distillate showed the reactions of benzyl alcohol. (a) It was oxidized by treatment with chromic anhydride to benzaldehyde, which was converted into benzaldehydephenylhydramne, when treated with phenylhydrazine, according to the method described by Mulliken.[14] The product of the reaction melted at 155–156°; this is the melting point of the hydrazone obtained by treatment of benzyl alcohol of known purity, first with chromic anhydride and then with phenylhydrazine. (b) It reacts with 3-nitrophthalic anhydride to form an α-monobenzyl ester, $C_6H_3\overset{3}{(NO_2)}\overset{1}{(COOH)}\overset{2}{(CO_2CH_2C_6H_5)}$. Our ester

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[11] Ref. 3, p. 543.

[12] Fifty per cent. sulfuric acid was chosen since acid of greater strength charred the salt, while acid weaker than fifty per cent. formed a yellow jelly-like substance. Hydrocyanic acid was invariably evolved, regardless of the strength of the acid used.

[13] Houben-Weyl, "Die Methoden der Organischen Chemie," G. Thieme, Leipzig, 1921, Vol. I, p. 238.

[14] Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 168.

showed the melting point of pure 3-nitrophthalic-a-monobenzyl ester, 175°. The melting point of a mixture of our ester and 3-nitrophthalic-a-monobenzyl ester of known purity was 175°. By the decomposition of 10 g. of sodiumphenylacetonitrile, 4 g. of benzyl alcohol was obtained, or 52% of the amount required by Equation 5.

Substitution Reactions.—Sodiumphenylacetonitrile was alkylated by treatment of a suspension of the salt in dry ether with an excess of ethyl iodide. The reaction was allowed to continue for several days at room temperature, and the reaction mixture was finally heated under reflux for an hour. The largest yield of the reaction product, a-phenylbutyronitrile, so far obtained is 10%. The unused sodium salt remained suspended in the ether mixed with white sodium iodide formed in the reaction. The effort will be made to increase the yield by modifications of the method described.

2. α-Sodium-α-phenylbutyronitrile, $(C_6H_5)(C_2H_5)C{=}C{=}NNa$ or $(C_6H_5)(C_2H_5)(CN)CNa$.—α-Sodium-α-phenylbutyronitrile was prepared by a method described in detail in the earlier report of the authors.[3] Analyses of the salt proved its purity.

Anal. Subs., 0.2577, 0.1336: Na_2SO_4, 0.1098, 0.0567. Calcd. for $NaC_{10}H_{10}N$: Na, 13.76. Found: 13.80, 13.75.

Behavior with Acid. (1) Determination of Hydrocyanic Acid.—Treatment of a-sodium-a-phenylbutyronitrile with cold sulfuric acid produced hydrocyanic acid, exactly as in the case of sodiumphenylacetonitrile. The amount formed was determined quantitatively by the method used for sodiumphenylacetonitrile.

Anal. Subs., 0.8441, 0.8577: 50.45, 51.15 cc. of 0.1 *N* $AgNO_3$, factor 0.9928. Calcd. for $NaC_{10}H_{10}N$: CN, 15.56. Found: 15.43. 15.39.

Thus the decomposition produced almost exactly the amount of hydrocyanic acid required by Equation 7.

(2) Identification of Diethylstilbene.—The other product of decomposition of α-sodium-α-phenylbutyronitrile with acid was a dark yellow solid of melting point 89–90°, readily separated from the sulfuric acid solution by filtration, which proved to be symmetrical diethylstilbene, $(C_6H_5)(C_2H_5)C{=}C(C_2H_5)(C_6H_5)$. The analytical data for this substance follow.

Anal. Subs., 0.1078, 0.2300: CO_2, 0.3608, 0.7698; H_2O, 0.0854, 0.1805. Calcd. for diethylstilbene, $C_{18}H_{20}$: C, 91.46; H, 8.53. Found: C, 91.28, 91.28; H, 8.80, 8.72.

The quantity of diethylstilbene formed from a-sodium-a-phenylbutyronitrile on treatment with acid was determined. From 0.8441 g. and 0.8577 g. of the salt 0.4140 g. and 0.4160 g. of diethylstilbene were obtained, respectively, or 68.6% of the amount demanded by Equation 8. It is probable that the yield will be nearer to that required by theory when larger quantities of salt are used for the decomposition. The identification of the compound was completed by its transformation into a dibromide by treatment with a solution of bromine in carbon tetrachloride. Bromine was slowly absorbed and the dark yellow color of diethylstilbene changed to a pale yellow. The dibromide melted with decomposition at 122–123°. Analysis for bromine by the Carius method gave the following results.

Anal. Subs., 0.8115, 0.6113: AgBr, 0.7762, 0.5866. Calcd. for $C_{18}H_{20}Br_2$: Br, 40.36. Found: Br, 40.70, 40.83.

Substitution Reactions.—The reaction of α-sodium-α-phenylbutyronitrile with chloroform ester in dry ether has been studied. The sodium atom of the salt is replaced by the group $-CO_2CH_3$, the product of the reaction being a-phenyl-a-cyanobutyric methyl ester, $(C_6H_5)(C_2H_5)C(CN)(CO_2CH_3)$. The cyano ester was isolated, its imino ester prepared and converted by hydrolysis into phenylethylmalonic dimethyl ester. These reactions are described in full detail in the earlier paper of Rising and Zee.[3]

Summary

1. A new field of investigation of nitride-carbide tautomerism is outlined.
2. The sodium salt of phenylacetonitrile and that of α-phenylbutyronitrile have been prepared. Their behavior with acid suggests the nitride structures $[(C_6H_5)HC{=}C{=}N^-]Na^+$ and $[(C_6H_5)(C_2H_5)C{=}C{=}N^-]Na^+$ for the two salts.
3. The behavior of the salts in substitution reactions suggests for them carbide structures $[(C_6H_5)(CN)HC^-]Na^+$ and $[(C_6H_5)(C_2H_5)(CN)C^-]Na^+$.
4. The "double behavior" of the salts indicates a tautomeric relationship between the nitride and carbide forms.
5. The salts are considered to be unstable intermediate products in the aldol-like condensation reactions described by E. von Meyer.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

THE USE OF THE CARIUS METHOD FOR THE DETERMINATION OF SULFUR IN THE LESS VOLATILE PETROLEUM OILS[1]

BY JOHN M. DEVINE[2] AND F. W. LANE[3]

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Largely because of the tedious and difficult technique involved, the Carius method has been shunned in the determination of sulfur in petroleum, although it is the method recognized as standard by most organic analysts. It is inapplicable to low sulfur oils, as the relatively small sample that must be used gives an amount of barium sulfate that is not readily handled. When the greatest accuracy is required in the determination of sulfur in petroleum oils containing 0.5% or more of this element, the Carius method must presumably be used.

To insure complete decomposition of petroleum oils, the procedure usually applied to organic compounds needs some revision with regard to weight of sample, quantity of fuming nitric acid and method of heating. Such changes are also necessary because the percentage of sulfur, even in high sulfur petroleums, is much less than is usually found in the average organic substance. Mabery and Smith[4] noted that certain conditions must be observed if the method is to give accurate results with sulfur containing petroleum oils. Unfortunately they failed to state these conditions fully or to present data from which the accuracy of their statements could be judged.

It is believed, therefore, that the experimental conditions worked out

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[4] Mabery and Smith. Am. *Chem.* J., 16, 84 (1894).

by the writers while making many sulfur determinations by the Carius method will prove helpful to others desiring to use the method under similar conditions. The procedure outlined below is not intended to be complete in detail, as a very full account can be found in the excellent book by Gattermann.[5] It attempts only to set forth and emphasize the conditions essential to success with petroleum oils of the less volatile type containing over 0.5% of sulfur.

Method

Weigh accurately a sample of oil of approximately **0.25** g. into a glass tube about 4 inches long and of 1/4-inch bore. By means of a long stemmed funnel, introduce into a Carius bomb tube[6] 4 cc. of pure fuming nitric acid. Allow the tube containing the sample to slide slowly down into the acid, taking care that there is no contact between oil and acid. Seal the Carius tube in the usual manner[7] and place in the furnace.

Increase the temperature of the furnace gradually, during a period of seven hours, from room temperature to **175°**. Cut off the heat. When the tube is thoroughly cool, hold the capillary cautiously in a luminous flame to drive back any liquid which has accumulated there. Then place the extreme end of the capillary in a hot flame to release the pressure. Reseal, replace in the furnace and resume heating. Bring the temperature rapidly to 175° and then increase to 225° gradually during the succeeding seven hours. Stop the heating and release the pressure as before. Again resume heating; bring the temperature quickly to 225° and then increase gradually during the succeeding seven hours to 300°. Release the pressure. The heating is now complete.[8]

Mark with a file the end of the tube bearing the capillary, break the tube and transfer the contents together with the washings to a 400-cc. beaker. The total volume should not be in excess of 250 cc.

Filter through a qualitative paper and wash the filter three times. Place on a hot-plate and evaporate to a volume of **5** to **10** cc.; transfer to a steam-bath for four hours, or longer if necessary. to remove nitric acid.[9]

Add 75 cc. of water and **5** drops of hydrochloric acid (sp. gr., **1.18)** and bring to boil. Add 10 cc. of a hot 10% solution of barium chloride drop by drop, with constant stirring. Keep the solution hot for one hour, subsequently allowing it to stand for twelve hours. Filter through an ashless filter paper, ignite and calculate the percentage of sulfur from the weight of the barium sulfate precipitates.[10]

Experimental

Sulfur (flowers) was dissolved in white, sulfur-free[11] medicinal oil to give an oil containing approximately 0.49% of sulfur. A large number

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[5] Gattermann, "The Practical Methods of Organic Chemistry," translated by Schober and Babasinian, The Macmillan Co., New York, 1921, 3rd American ed.

[6] The type used is made of heavy-walled, soft glass tubing provided with a constriction near the open end; length, **70** cm.; diameter outside, **22** mm.; obtainable from most of the chemical laboratory supply houses.

[7] Ref. 5, p. 63.

[8] The contents of the tube should show no evidence of undecomposed oil or free carbon. The liquid will be clear and dark green to pale green.

[9] Scarcely any signs of liquid will remain in the beaker.

[10] A blank is run by adding 4 cc. of fuming nitric acid to 250 cc of water and carrying through as a regular determination.

[11] Containing less than 0.01% of sulfur.

of determinations indicated that 0.4 g. of this oil required approximately 4 cc, of fuming nitric acid for its decomposition under the experimental conditions. The use of larger amounts of sample or acid almost invariably led to explosion of the tubes.

In the first set of Carius determinations successfully completed, these proportions of the prepared sulfur oil and acid were used. The heating was conducted as directed in the method except that the heating periods were of four hours' duration. Upon cooling, the contents of the tubes were light green and clear. To all appearance decomposition was complete.

The contents of the respective tubes were washed into 400-cc. beakers, filtered and evaporated to a volume of 75 cc. Precipitation of the sulfate was brought about in the usual manner by addition of a hot 10% solution of barium chloride. After filtering and igniting, the following results were obtained: 0.480, 0.491, 0.522, 0.501 and 0.517% of sulfur; average, 0.502%.

The variation between individual results was considered much too great. It seemed likely that the error resulted from the interference of nitric acid; but even evaporation to a "small volume" before precipitation, as recommended by Treadwell-Hall,[12] did not remove the acid completely enough. Evaporation to small volume (10 cc.) on the hot-plate, followed by heating on the steam-bath until the beakers were practically "dry" led to satisfactory results.

Another set of Carius determinations was made on the prepared sulfur oil, using 0.4 g. of oil, 4 cc. of pure fuming nitric acid and three four-hour periods of heating as outlined above. The washings were evaporated almost to "dryness" as just described, 75 cc. of water was added, then five drops of hydrochloric acid (sp. gr., 1.18) and precipitation brought about as before. The results were as follows: 0.477, 0.481, 0.481, 0.482 and 0.482% of sulfur; average, ±0.481%. These results were considered satisfactory.

The next step involved the use of an oil in which the sulfur (approximately 2.5%) occurred naturally.[13] A set of determinations was made on this oil using a 0.4g. sample, 4 cc. of fuming nitric acid and heating for three four-hour periods. The washings were evaporated to "dryness" on the steam-bath and the following results were obtained: 2.38, 2.40, 2.31, 2.41 and 2.44% of sulfur; average, ±2.39%.

Although the agreement of the individual results was fairly good, it remained to be shown beyond a reasonable doubt that oxidation was complete. Accordingly, a set of determinations was made on the same oil using

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[12] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, Vol. II, 6th ed., revised, 1924, p. 326.

[13] The oil used in this work was extracted from a heavier oil by means of 95% ethyl alcohol. Its properties were: sp. gr. $\frac{37.7^\circ}{15.6^\circ} = 0.948$; viscosity at 37.7° = 2.592 Poises; $S = 2.55\%$.

only a 0.25g. sample. The use of 4 cc. of fuming nitric acid and three four-hour heating periods was retained. The results were: 2.46, 2.47, 2.41, 2.48, 2.49 and 2.40% of sulfur; average, ± 2.45%.

Since this average was materially higher than the previous one (2.39% S) it seemed possible that oxidation was still incomplete. It was impracticable to decrease the weight of sample below 0.25 g. or to increase the volume of fuming nitric acid above 4 cc. The time of heating was accordingly increased. A set of determinations was run, using a 0.25g. sample, 4 cc. of fuming nitric acid and heating for three seven-hour periods, the same temperature intervals as before being retained. The pressure was released at the end of each period. The results were: 2.52, 2.51, 2.55 and 2.50% of sulfur; average, 2.52%. Since this figure showed still an appreciable gain over the preceding one (2.45% S), another set of determinations was made in which the heating was increased to three fifteen-hour periods. The other conditions remained unchanged. The results were: 2.61, 2.54, 2.51, 2.57, 2.59 and 2.50% of sulfur; average, ± 2.55% S. As this figure agrees with the preceding one (2.52% S) within the experimental limits of the method, it was assumed that the three seven-hour heating periods were sufficient to decompose the oil completely.

There appears to be no way of checking the absolute accuracy of this result, as almost nothing is known concerning the sulfur compounds in the lubricating fractions of petroleum. The statement is sometimes found in textbooks that sulfones resist decomposition by fuming nitric acid and when present in Carius sulfur determinations lead to low results. Accordingly, the sulfur in a carefully purified sample of n-butyl sulfone was determined by the method outlined above. The results were: 18.16, 18.27, 18.23 and 18.17% of sulfur; average, 18.21%. Calcd. for *n*-butyl sulfone, 17.99. With this sulfone, therefore, there seems to be no difficulty in determining sulfur with a proper degree of accuracy.

Summary

Specific directions are given for use of the Carius method to determine sulfur in the less volatile petroleum oils. Especial care is necessary to effect complete oxidation. Nitric acid is completely removed before the barium sulfate is precipitated.

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 174]

SOME DERIVATIVES OF *n*-HEPTANE

BY ROBERT T. DILLON AND HOWARD J. LUCAS

RECEIVED FEBRUARY 15, 1928 PUBLISHED JUNE 5, 1928

Introduction

Following the line of reasoning previously employed in the case of 2-pentene and hydrogen bromide[1] it would be predicted that the addition of hydrogen bromide to 3-heptene should yield 3-bromoheptane largely, whereas on the basis of an alternately polarized carbon chain the product should be 4-bromoheptane. The test of this question necessitated first the preparation of these two compounds and they have been found to be so similar in physical properties that unfortunately no differentiation could be made between them. It was not considered profitable to make use of any addition reaction which would necessitate subjecting the products to a subsequent reaction, such for example as the addition of sulfuric acid and the hydrolysis of the resulting hydrogen alkyl sulfate to the alcohols, since this would necessitate a separate and complete study of each of the reactions. In the accompanying table are given the physical constants of pairs of isomers which might be of possible use in solving the problem.

TABLE I

PHYSICAL CONSTANTS

Compound	B. p., °C. (corr.)	M. p., °C.	Density, d_4^{25}	Refractive Index n_D^{20}	Refractive Index n_D^{25}
3-heptanol	152 7–154 (745)	...	0.8159	1.4201	1.4175
4-heptanol	153.4–154.3 (745)	−41.5 to −37.2	.8175	1.4199	1.4173
3-chloroheptane	143.4–144.4 (751)	...	...	1.4237	....
4-chloroheptane	143.1–144.4 (751)	...	...	1.4237	....
3-bromoheptane	84.5–85.5 (74)	...	...	1.4507	....
4-bromoheptane	84.0–85.5 (72–73)	...	...	1.4506	....

The compounds were slowly fractionated from flasks with attached side arms of the Eastman type until the boiling range was that indicated and the refractive index, taken with an Abbé refractometer, suffered no further change. The heating curves were obtained by allowing each substance, surrounded by a carbon dioxide–alcohol bath in a Dewar flask, to warm slowly while agitation was carried on. Temperatures read by means of a thermocouple were plotted against time. In only one case, 4-heptanol, was a freezing point value obtained. The other substances formed glasses which, even when cooled with liquid air over a period of several days, failed to crystallize.

The closeness with which the pairs of isomers approximate each other as far as the boiling points and refractive indices are concerned indicate that

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[1] Lucas and Moyse, THIS JOURNAL, 47, 1459 (1925).

the 3- and 4-positions in n-heptane are practically equivalent, a condition which renders the analysis of mixtures of isomers difficult. It was hoped that the melting points would be quite dissimilar since the 3-derivatives are the less symmetrical and should on that account possess lower melting points. The failure to obtain other than glasses with all but the 4-heptanol, and the four degree range of the latter may point to the presence of impurities in the compounds. If small amounts of impurities prevent crystallization, the prospect of crystallizing a mixture of any of the above pairs of heptyl derivatives would appear to be remote. The conversion of the isomeric halides to solid compounds and the analysis of the resulting mixture through separation of the solids does not appear feasible since the quantitative conversion of secondary halides to solid compounds is a difficult matter, due to the ease with which the unsaturated hydrocarbon is produced. This was found to be the case when they were allowed to react with the silver salt of 3,5-dinitrobenzoic acid.

The synthesis of the two alcohols by means of magnesium alkyl halides and ethyl formate led to the observation that only symmetrical disubstituted methanols can be obtained by this means. This conclusion could almost be predicted from the observation that a two-fold excess of ethyl formate over the magnesium alkyl halide is necessary in preparing aldehyde~. In the attempted synthesis of 3-heptanol the ethyl formate was allowed to react first with ethyl magnesium bromide and then with butyl magnesium bromide. The products of the reaction were diethylmethanol and dibutylmethanol, with hardly a trace of the desired ethylbutylmethanol.

Experimental

Preparation of **4-Heptanol.**—This alcohol was prepared in a 63% yield by using 370 g. (3 moles) of n-propyl bromide[3] (b. p. 68.2–69.2°), 72 g. (3.1 moles) of magnesium turnings (Eastman), 110 g. (1.5 moles) of ethyl formate (distilling at 52.0–53.4° from phosphorus pentoxide) and 650 g. (9 moles) of anhydrous ether. After two fractionations at 745 mm. pressure, the alcohol distilled at 153.4–154.4° (corr.) and had the following constants: ▼ ▼. p. –37.2 to –41.5°; d_4^{25} = 0.8175; n_D^{20} = 1.4199; n_D^{25} = 1.4173.

Preparation of **3-Heptanol.**—The attempted synthesis of this alcohol from 109 g. (1 mole) of ethyl bromide, 54 g. (2.24 moles) of magnesium, 74.1 g. (1 mole) of ethyl formate, 184 g. (1 mole) of *n*-butyl iodide and 444 g. (6.0 mole) of ether in accordance with the following reactions

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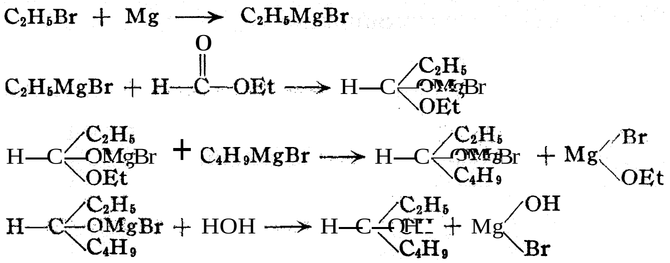
[2] Gattermann and Maffezzoli, *Ber.*, 36, 4152 (1903); Williams, J. *Chem. Soc.*, 89,273 (1906).

[3] Prepared in 76% yield from *n*-propyl alcohol (Eastman's, b. p. 96–98°), sodium bromide and concentrated sulfuric acid, similar to the preparation of butyl bromide, "Organic Syntheses," Vol. I, John Wiley and Sons, Inc., New York, 1921.

[4] Values previously given are: b. p. 149–150°, Kurtz, Ann., 161, 212 (1872); 154–155°, Willcox and Brunel, THIS JOURNAL, 38,1838 (1916); 155°, Brunel, *ibid.*, 45, 1338 (1923); d_4^{25} = 0.8129 (B); d_{25}^{25} = 0.814 (K); n_D^{25} = 1.4178 (B).



$$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$$

$$C_2H_5MgBr + H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OEt \longrightarrow H{-}C{\begin{smallmatrix} C_2H_5 \\ OMgBr \\ OEt \end{smallmatrix}}$$

$$H{-}C{\begin{smallmatrix} C_2H_5 \\ OMgBr \\ OEt \end{smallmatrix}} + C_4H_9MgBr \longrightarrow H{-}C{\begin{smallmatrix} C_2H_5 \\ OMgBr \\ C_4H_9 \end{smallmatrix}} + Mg{\begin{smallmatrix} Br \\ OEt \end{smallmatrix}}$$

$$H{-}C{\begin{smallmatrix} C_2H_5 \\ OMgBr \\ C_4H_9 \end{smallmatrix}} + HOH \longrightarrow H{-}C{\begin{smallmatrix} C_2H_5 \\ OH \\ C_4H_9 \end{smallmatrix}} + Mg{\begin{smallmatrix} OH \\ Br \end{smallmatrix}}$$

gave, instead of the expected alcohol, a mixture of diethylmethanol (3-pentanol) and dibutylmethanol (5-nonanol). In order to avoid an excess of the Grignard reagent the ethereal solution of the ethylmagnesium bromide was added to the ethyl formate and then the butylmagnesium bromide added to the resulting product. Two fractional distillations of the final product gave no 3-heptanol but yielded instead 27.4 g. (0.311 mole) of impure 3-pentanol, b. p. 105–120°, and 49.5 g. (0.345 mole) of impure 5-nonanol, b. p. 76–80.6° at 10 mm., corresponding to yields of 62 and 69%, respectively, calculated on the basis of separate reactions. Some pure 5-nonanol was prepared from ethyl formate and n-butylmagnesium bromide and was found to distil at 77–79.5° under a pressure of 10 mm.[5]

The desired alcohol was obtained in 40% yield from 155 g. (1.1 moles) of butyl bromide, ~~b. p. 99.1–100°, 27.5 g. (1.1 moles) of magnesium turnings~~ (Eastman), 65.6 g. (1.1 moles) of propionic aldehyde,[6] b. p. 45.5–50.5°, and 500 g. (68 moles) of ether. After three fractionations there was obtained a total of 53 g. of product (40% yield) having the following characteristics: b. p. = 152.3–156" (corr.) at 745 mm.; d_4^{25} = 0.8159; n_D^{20} = 1.4197; n_D^{25} = 1.4185. When this was still further purified by subsequent distillations the properties were changed as follows:[7] b. p. = 152.7–154° (corr.) at 745 mm. and n_D^{20} = 1.4201.

Preparation of **the Heptyl Halides.**[8]—The 3-chloro- and 4-chloroheptanes were prepared from the corresponding alcohols by the method of Norris and Taylor[9] in yields of 30 and 35%, respectively, and the bromo derivatives were obtained by heating each alcohol with four times the calculated quantity of hydrobromic acid (sp. gr. = 1.49) under a reflux cooler for one and one-half hours and then distilling the bromide. The yields were 30 and 40%, respectively. In each case the halide, after washing with cold, concd., sulfuric acid and water, was dried with anhydrous potassium carbonate, first by shaking with a small amount and removing the heavier aqueous phase which developed, and then by letting it stand with an additional amount of the solid. Since the isomeric chlorides and bromides have almost identical properties, and on that account cannot be easily distinguished, the preparation of 3-heptene and its reaction with a hydrogen halide was not attempted.

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[5] Malengreau, Chem. Cent., 1907, I, 1398, states that 5-nonanol distils at 193° under a pressure of 766 mm.

[6] Obtained in 30% yield by the oxidation of n-propyl alcohol with sodium dichromate and sulfuric acid, drying the product with potassium carbonate and fractionating three times.

[7] Blaise and Picard, *Ann. chim. phys.*, [8] 26, 287 (1912), report the boiling point as 156.5–157°, and Pickard and Kenyon, J. Chem. *Soc.*, 103, 1943 (1913), as 150–2°.

[8] Subsequent to the completion of this work it has been noted that the chloride and bromide of 4-heptanol have been prepared by Mathus and Gibon, Bull. *soc.* chim. *Belg*, 34, 303 (1925).

[9] Norris and Taylor, THIS JOURNAL, 46, 753 (1924).

Summary

Some physical properties of the pairs of isomers, 3- and 4-heptanol, 3- and 4-chloroheptane and 3- and 4-bromoheptane have been determined. The boiling points and refractive indices of any pair are very similar, while of only one substance, 4-heptanol, could a freezing point be obtained. The reaction of ethyl formate with butyl magnesium bromide and ethylmagnesium bromide gave 2-pentanol and 4-nonanol but no 3-heptanol.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A METHOD FOR THE QUANTITATIVE ANALYSIS OF LEAD IN ORGANIC COMPOUNDS

BY HENRY GILMAN AND JACK ROBINSON

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In connection with studies on organolead compounds a need was felt for a convenient method for the quantitative estimation of total lead in compounds having an aryl group attached directly to lead. None of the present methods was found satisfactory for our purposes. The method described here consists essentially in the decomposition of the sample by sulfuric and nitric acids, and estimation as lead sulfate. It has been used successfully by different workers in this Laboratory for the analysis of various aryl and aryl-alkyl lead compounds.

Polis[1] analyzed his organolead compounds, as lead sulfate, after decomposition by concentrated sulfuric acid and oxidation by potassium permanganate. Griittner and Krause[2] decomposed their compounds with a 30% solution of bromine in carbon tetrachloride, and estimated the lead as lead bromide. They also used the Carius method of decomposition for volatile compounds. Calingaert[3] modified the method of decomposition by bromine, and obtained highly satisfactory results with *alkyl* lead compounds. This method, with our compounds, has not given acceptable analyses, very probably because of the greater firmness of attachment of *aryl* groups to lead.[4] Treadwell and Hall[5] recommend decomposition in a crucible by concentrated sulfuric acid and weighing as lead sulfate. We have not obtained consistent results by this method,

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[1] Polis, *Ber.*, 19, 1024 (1886); 20, 718 (1887).

[2] Griittner and Krause, Ber., 49, 1125 (1916).

[3] Calingaert, *Chem. Reviews*, 2, 43 (1925).

[4] Dr. Calingaert has found that the aryl lead compounds submitted by us to him for a comparative rating of their antiknock effectiveness can be analyzed satisfactorily by heating with concentrated nitric acid subsequent to treatment with bromine in carbon tetrachloride.

[5] Treadwell and Hall, "Analytical Chemistry" (5th English edition), John Wiley and Sons, Inc., New York, 1919, Vol. II, p. 175.

probably because of loss due to spattering. The procedure adopted by us is a slight modification of the general treatment suggested by Noyes and Bray[6] for the decomposition of organic matter in a sample to be prepared for qualitative analysis.

The analysis described here has not been used with volatile organolead compounds having only alkyl groups attached to lead. Such compounds are readily analyzed by the bromine method[2,3] and it is quite likely that a special technique would be needed with the nitric and sulfuric acid treatment to avoid loss by spattering.

Method of Analysis

About 0.5 g. of sample is placed in a 400-cc. Pyrex beaker (or casserole of about the same size) and to this is added 7.5 cc. of concentrated sulfuric acid. The beaker is covered with a watch glass and very gently warmed over a small flame. A too vigorous reaction can be avoided by removing the beaker and agitating by a rotatory motion when the first indication of reaction appears (about 50–90°). The process of mild warming, removal from flame and gentle stirring is repeated until the white precipitate of lead sulfate settles out and none of the sample remains suspended in the sulfuric acid. The contents are then gradually heated until white fumes are copiously evolved.

After cooling to about 80°, 1–1$^1/_2$ cc. of concentrated nitric acid (sp. gr., 1.42) is added; heat is again applied, gently at first; and, when any vigorous evolution of nitrogen oxides has ceased, the watch glass is removed and the beaker heated until copious white fumes are evolved. One cc. of concentrated nitric acid is added, after cooling the beaker and contents, and the heating is then repeated to the evolution of white fumes. By these operations, the organic matter is totally oxidized when the acids have been sufficiently heated; and the lead sulfate is dissolved completely in the hot concentrated sulfuric acid.

The solution is cooled to about 30° and any material adhering to the sides of the beaker is washed down with 5–10 cc. of distilled water. After slight agitation to mix the water and acids, the mixture is again heated to the evolution of white fumes. The evaporation may cause bumping if done over a flame, but this may be avoided by heating on the ordinary 220-volt electric hot-plate, with the heat on "low." The beaker is then heated strongly to remove all nitric acid, after which it is cooled, more water is added and the operations through strong heating are repeated.

To the cooled beaker there is then added 150 cc. of water and 100 cc. of 95% alcohol. After standing for one hour, the precipitate is filtered through a Gooch crucible, washed with 10% sulfuric acid and then with 95% alcohol to remove all of the sulfuric acid. The crucible and contents

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[6] Noyes and Bray, THIS JOURNAL, 29, 144 (1907).

are then dried, in the customary manner, by heating for one hour at 110°, and weighed as lead sulfate.

The results of a few representative analyses follow.

TABLE I

RESULTS OX ANALYSES

	% Pb		
Compound	Calcd.	Pound	
Tetraphenyl lead	**40.18**	**39.83**	**40 03**
Tetra-*p*-bromophenyl lead	**24.91**	**24.68**	**24.38**
Diphenyl-di-*p*-bromophenyl lead	**30.76**	**30.65**	**30.80'**
Triphenyl-*n*-butyl lead	**41.82**	**41.52**	**41.46**
Diphenyl-di-isobutyl lead	**43.58**	**43.08**	**43.53**

The authors wish to acknowledge helpful suggestions from Dr. J. A. Wilkinson.

Summary

A method is described for the quantitative estimation of total lead in non-volatile organolead compounds by decomposition with concentrated sulfuric and nitric acids.

AMES, IOWA

[CONTRIBUTION PROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE THERMAL DECOMPOSITION OF NITRITES. THE NITRITES OF TRIPHENYLETHYLAMINE AND DIPHENYLETHYLAMINE[1]

BY LESLIE HELLERMAN, MAURICE LEON COHN AND REU EVERETT HOEN

RECEIVED FEBRUARY 23, 1928 PUBLISHED JUNE 5, 1928

That the action of nitrous acid upon a primary aliphatic amine does *not* in general produce *exclusively* the alcohol of corresponding structure, has been pointed out by a number of investigators; an impression to the contrary regarding this fundamental class of organic reactions appears, nevertheless, to be held by many. In view of this and of the experimental results to be reported in this paper, it will not be out of place to include a few references[2] to researches which may in themselves be held to have demonstrated strikingly that *if conversion of an amine to an alcohol of corresponding structure be considered the "normal" course of the action, then*

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[1] This paper is based in part upon dissertations submitted to the University of Chicago by Maurice Leon Cohn and Reu Everett Hoen, in partial fulfilment of the requirements for the degree of Master of Science. An account of some of the work herein reported was presented before the Seventh Midwest Regional Meeting of the American Chemical Society at Chicago, May, 1927.

[2] (a) Meyer and Forster, Ber., **9,** 535 (1876); (b) Demjanow, Ber , **40,** 4393 (1907); (c) Wallach, Ann., **353,** 318 (1907); **359,** 312 (1908); (d) Henry, *Compt.* rend., **145,** 899 (1907); (e) Jeffreys, Am. *Chem.* J., 22, 36 (1899).

it must be said *that* observations of "abnormal" results *have* ***been*** at least as *numerous* as of the "normal." Certain of such "abnormal" results will be considered briefly in the sequel.

It has been observed in the present work that the action of heat upon an aqueous suspension of the nitrite[3] of β,β,β-triphenylethylamine[4] results in the production of triphenylethylene, $(C_6H_5)_2C{:}CH(C_6H_5)$, as the principal product of the reaction. The action of heat upon the nitrite in the dry state gives the same product together with a small amount of β,β,β-triphenylethylammonium nitrate.

For the interpretation of the course of these interesting changes, it has been considered most plausible to assume tentatively the series of reactions (involving the diazotization of β,β,β-triphenylethylamine) which are represented by the following equations.

$$(C_6H_5)_3CCH_2NH_3ONO \rightleftharpoons (C_6H_5)_3CCH_2NH_2 + HONO \qquad (1)^5$$

$$(C_6H_5)_3CCH_2NH_2 + HONO \longrightarrow HOH + (C_6H_5)_3CCH_2NHNO\ [\rightleftharpoons (C_6H_5)_3CCH_2N_2OH] \qquad (2)$$

$$(C_6H_5)_3CCH_2N_2OH \longrightarrow (C_6H_5)_3CCH(N_2) + HOH \qquad (3)$$

The production of a diazo derivative by means of the action of nitrous acid upon an a-amino acid ester constitutes a rather well-developed method of synthesis; and there exists a conspicuous example of the isolation of a diazo derivative from the action of nitrous acid upon an amine of the type RCH_2NH_2: amino-acetophenone, $C_6H_5COCH_2NH_2$, yields diazo-acetophenone, $C_6H_5COCH(N_2)$.[6]

Triphenyldiazo-ethane,? if formed as assumed, would undoubtedly possess the property exhibited by other compounds of its type of losing nitrogen under the influence of heat. A reactive, unstable, bivalent carbon (methylene) derivative, triphenylethylidene, might result. The rearrangement of a phenyl group to the reactive bivalent carbon atom would represent the final step in the series of reactions which lead to triphenylethylene. Thus, we may have

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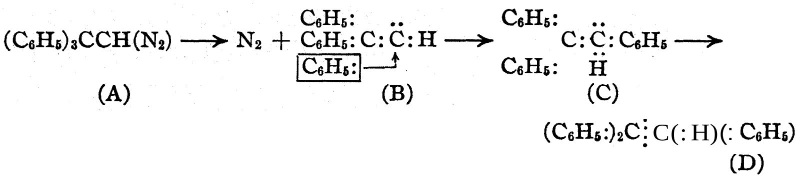
[3] The salt is surprisingly stable at room temperatures (compare the experimental part). With the exception of γ,γ,γ-triphenylpropylammonium nitrite, recently prepared in this Laboratory by Hellerman and Sudzuki (unpublished work), this is probably the only nitrite of an amine of Type RCH_2NH_2 which has been isolated. The isolation of nitrites of primary amines of other types (for example, $RR'CHNH_2$) has been reported by Noyes, Am. Chem. *J.*, 15, 539 (1893); *ibid.*, 16,449 (1894), and by Wallach, Ann., 353, 318 (1907).

[4] Hellerman, THIS JOURNAL, 49, 1735 (1927).

[5] The presence of nitrate ion in the reaction mixture may be assumed, since nitrous acid and its decomposition products are by-products of the reaction. We may have $3HNO_2 \longrightarrow H^+ + NO_3^- + 2\,NO + H_2O$. This accounts for the appearance of β,β,β-triphenylethylammonium nitrate when the nitrite is heated in the dry state.

[6] See Houben-Weyl, "Die Methoden der Organischen Chemie," Georg Thieme, Leipzig, 1924, Vol. 4, p. 645, for references to the literature.

[7] A research involving the preparation of triphenyldiazo-ethane and the study of its properties is planned.



$$\underset{(A)}{(C_6H_5)_3CCH(N_2)} \longrightarrow N_2 + \underset{(B)}{\begin{array}{c} C_6H_5:\ \ \cdot\cdot \\ C_6H_5:C:\overset{\cdot\cdot}{C}:H \\ \boxed{C_6H_5:}\nearrow \end{array}} \longrightarrow \underset{(C)}{\begin{array}{c} C_6H_5: \\ C:\overset{\cdot\cdot}{C}:C_6H_5 \\ C_6H_5:\ \ \underset{\cdot\cdot}{H} \end{array}} \longrightarrow \underset{(D)}{(C_6H_5:)_2C\vdots C(:H)(:C_6H_5)} \quad (4)^{8}$$

This formulation implies, of course, that the phenyl group, together with the electron pair (:) which was shared between it and the adjoining carbon atom in (B), "migrates" to the bivalent carbon atom; the octet of the latter is thus completed and the immediate cause of instability removed. The rearrangement would leave the carbon atom bearing two phenyl groups in (C) "positive"[9] with respect to that which gained a phenyl group; finally, we should have the shift of an electron pair which results in the formation of the electronically more symmetrical, "stable" form of the olefin (D).

In the light of the observations recorded above and of the hypothesis which has been developed to interpret them, the essential nature of several rather mystifying reactions (involving the action of nitrous acid upon primary amines) which have been recorded in the literature, becomes less obscure. Thus, the action of nitrous acid upon trimethylethylamine, $(CH_3)_3CCH_2NH_2$, in the presence of water was found by Freund and Lenze[10] to yield dimethylethylcarbinol, $(CH_3)_2(C_2H_5)COH$, and these investigators concluded that trimethylethanol, $(CH_3)_3CCH_2OH$, was formed first, and then, simply, the hydroxyl group and a methyl group exchanged positions. A much more reasonable explanation results if it is assumed that trimethylethylene in a "reactive" form is an intermediate product and this product absorbs water. $H^+(OH)^-$ is added in the direction required by the polarity of the olefinic "double bond," the assumed origin of that polarity being indicated clearly by the following formulation[11]

[8] The role played here by the hypothetical intermediate (B) would be entirely analogous to that assumed by Professor Stieglitz for univalent nitrogen derivatives, R_3CN, in rearrangements of compounds of the types, R_3CNHX, $R_3CN(N_2)$, etc., which have been extensively investigated by Stieglitz and his collaborators. See, for example, Stieglitz and Stagner, THIS JOURNAL, 38, 2046 (1916). See also Jones and Hurd, *ibid.*, 43, 2422 (1921). Compare Hellerman and Sanders, ibid., 49, 1745 (1927).

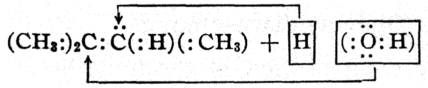
[9] See ref. 11.

[10] Freund and Lenze, *Ber.*, 24, 2150 (1891). They were attempting to prepare β,β,β-trimethylethanol and observed the "abnormal" result cited.

[11] It is apparent that the appearance of an intermediate complex, $RR'R''CCH<$, where the R's represent groups or hydrogen atoms, may well account for the various types of products which have been obtained in reactions of this type (compare reference 2). The complex may add, at the bivalent carbon atom, water or unchanged primary amine, yielding, respectively, the alcohol of corresponding structure or the secondary amine (isolated as nitroso derivative). If, instead, the bivalent carbon atom is "saturated" by means of rearrangement of a group or hydrogen atom, R, an olefin, $R'R''C{=}CHR$, results If, however, water has been added by the olefin in "reactive" form, an

$$(CH_3)_3CCH_2NH_3ONO \longrightarrow (CH_3)_3CCH(N_2) + 2H_2O \qquad (5)$$

$$(CH_3)_3CCH(N_2) \longrightarrow N_2 + (CH_3{:})_3C{:}\ddot{C}{:}H \longrightarrow (CH_3{:})_2C{:}\ddot{C}({:}H)({:}CH_3) \qquad (6)$$



$$(CH_3{:})_2C{:}\ddot{C}({:}H)({:}CH_3) + \boxed{H}\ \boxed{({:}\ddot{\underset{\cdot\cdot}{O}}{:}H)} \longrightarrow (CH_3)_2(HO)CCH_2(CH_3) \qquad (7)$$

To what extent water will he added as the final step in reactions of the type under discussion as in the case just cited, or the olefin itself produced, obviously may depend upon a number of factors such as the conditions of experiment (temperature, amount of water initially present, etc.), the solubility of the nitrite in water and the structural character of the "reactive" olefinic product of rearrangement. Triphenylethylene in its "reactive" state evidently does not add water (even when reaction is completed in aqueous suspension) but, instead, passes to its more stable form. On the other hand, it has been found here that in a related case involving the thermal decomposition of β,β-diphenylethylammonium nitrite in aqueous solution,[12] phenylbenzylcarbinol[13] is *a* product in high yield. Evidently the addition of water is involved here; the changes may be summed up as follows

$$(C_6H_5)_2CHCH_2NH_2 \xrightarrow[(HONO)]{} (C_6H_5)_2CHCH(N_2) \longrightarrow (C_6H_5)_2CHCH< \qquad (8)$$

$$(C_6H_5)_2CHCH< \longrightarrow (C_6H_5)\underset{|\quad|}{CHCH}(C_6H_5) \xrightarrow[HOH]{} C_6H_5CH(OH)CH_2(C_6H_5) \qquad (9)^{14}$$

When a mixture of equimolar parts of β,β-diphenylethylammonium chloride and sodium nitrite was heated in the dry state, stilbene, in 76% yield, was the product. This hydrocarbon is, of course, the expected product if it is considered that essentially β,β-diphenylethylammonium nitrite has been heated in the dry state.[15] In no event would phenylbenzylcarbinol be anticipated here, since this carbinol is known to become

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alcohol, $R'R''C(OH)CH_2R$, is the product. Assumption of rearrangement of R in effect as a negative group (that is, with the shared electron pair) has seemed highly consistent with the frequent observations of the appearance of an alcohol, $R'R''C(OH)CH_2R$.

[12] A solution of an equimolecular mixture of the amine hydrochloride and sodium nitrite was used; compare the experimental part.

[13] The same carbinol [Purgotti, *Gazz. chim. ital.*, (2) 23, 226 (1893)] is obtained when the nitrite of α,β-diphenylethylamine, $(C_6H_5)CH_2CH(C_6H_5)NH_2$, undergoes thermal decomposition. Purgotti actually sought to verify the structure of α,β-diphenylethylamine by means of this reaction. The risk attending the use of this type of reaction For the determination of structure of an amine is clearly seen in the experimental results herein reported.

[14] Other possible final products of the action were sought, but the only definite individual which could be isolated was phenylbenzylcarbinol. It is cleat, however, that a phenyl group, rather than the hydrogen atom, "migrated" largely. Probably the relative "electronegativity" [Kharasch and Marker, THIS JOURNAL, 48, 8130 (1926)] of competing groups determines largely to what extent they shall be involved in such rearrangements.

[15] Compare equation 4.

"dehydrated" to stilbene under conditions similar to those of this experiment (elevated temperature, presence of hydrogen ion).[16]

The Behavior of β,β-Diphenyldiazo-ethane

Of considerable interest from the point of view of the hypothesis employed in this paper for the interpretation of primary amine nitrite reactions is the behavior, observed under various conditions, of β,β-diphenyldiazo-ethane, $(C_6H_5)_2CHCH(N_2)$. It has been found that this substance,[17] when heated in the presence of dilute sulfuric acid, yields stilbene[18] as its decomposition product.

$$(C_6H_5)_2CHCH(N_2) \longrightarrow C_6H_5CH{=}CHC_6H_5 + N_2 \qquad (10)$$

When heated in the presence of neutral or alkaline media, the diazo compound is found to yield diphenylacetaldazine, together with indefinite, resinous matter. The latter observation is quite in accord with the known behavior of various well-described diazo derivatives[19] and the relationship between the facts here set forth may be adequately seen in the following: β,β-diphenyldiazo-ethane, when heated, may yield first nitrogen and the corresponding methylene derivative, $(C_6H_5)_2CHCH<$. The latter, in alkaline or neutral environment, in which it would be *slowly* formed in the presence of a large excess of diazo compound, may absorb unchanged β,β-diphenyldiazo-ethane with the formation of the aldazine.

$$(C_6H_5)_2CHCH< + N{\equiv}N{=}CHCH(C_6H_5)_2 \longrightarrow (C_6H_5)_2CHCH{=}N{-}N{=}CHCH(C_6H_5)_2 \qquad (11)$$

In the presence of acid, where (a) decomposition of the diazo compound would presumably be accelerated and (b) synthesis of the aldazine (a substance the hydrolysis of which is accelerated by acids) be rendered improbable, the bivalent carbon intermediate should rearrange largely to the olefin

$$(C_6H_5)_2CHCH< \longrightarrow (C_6H_5)CH{=}CH(C_6H_5) \qquad (12)$$

β,β-Diphenyldiazo-ethane has been assumed in the preceding section to be an intermediate product when nitrous acid acts upon β,β-diphenyl-

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[16] Compare (a) Limpricht and Schwanert, Ann., 155, 62 (1870); (b) Sudborough, *J. Chem. Soc.*, 67, 605 (1895).

[17] The substance, as prepared, was somewhat impure. Because of the experimental difficulties for attainment of high purity (compare the experimental part) and since the method of preparation and the properties of the compound left little doubt of its identity, it was deemed for the present purpose not necessary to expend further effort upon its purification. More extensive work upon diazo derivatives of the types, $RR'R''CCH(N_2)$ and $RR'CHCH(N_2)$, is in contemplation.

[18] Phenylbenzylcarbinol would not be expected; see the preceding section.

[19] See, for example, Staudinger, *Ber.*, 49, 1884 (1916), and other articles in the *Berichte*, 1916. In his interpretations of various transformations of aliphatic diazo derivatives. Staudinger has found the assumption of intermediate methylene derivatives to be decidedly useful.

ethylamine. In the latter case the diazo compound as *formed* would presumably be converted rapidly to the bivalent carbon complex, *rearrangement* of which, under the conditions, would evidently be a logical consequence.

Evidence for the Hypothetical Bivalent Carbon Intermediate: Synthesis of Triphenylacetaldehyde

Postulation of bivalent carbon complexes as intermediates in nitrite decompositions as has been done in this paper has seemed a logical step, especially since such complexes have already been assumed with considerable reason to be intermediates in various decompositions of aliphatic diazo compounds.[20] Several observations made in the course of this work appear to be decidedly in harmony with this type of hypothesis. It has been found that when β,β,β-triphenylethylammonium nitrite is heated with mercuric oxide, triphenylacetaldehyde, $(C_6H_5)_3CCHO$, appears as a product along with triphenylethylene.[21] Triphenylacetaldehyde would be a product if a transitorily existing intermediate, triphenylethylidene, were oxidized to the aldehyde very much as isocyanides, RNC< are oxidized under similar conditions to isocyanates.

$$(C_6H_5)_3CCH< + HgO \longrightarrow (C_6H_5)_3CCHO + Hg \qquad (13)$$

It was considered of importance in this connection to test the applicability of this type of procedure to the case of a well-described aliphatic diazo compound to which triphenyldiazo-ethane would be strikingly related structurally, namely, the azibenzil of Curtius.[22] Schroeter found[23] that the thermal decomposition of this interesting compound resulted in its rearrangement to diphenylketene.

$$C_6H_5COC(N_2)(C_6H_5) \longrightarrow C_6H_5CO\underset{A}{C}C_6H_5 \longrightarrow O{=}C{=}C(C_6H_5)_2 \qquad (14)$$

Of exceptional theoretical interest is the observation made in this work that azibenzil, heated in the presence of moist mercuric oxide, yields 74% of benzil, $C_6H_5COCOC_6H_5$. This would, of course, be the expected product if, in the presence of mercuric oxide, "saturation" (that is, ultimate completion of the octet)[24] of the bivalent carbon atom in the assumed intermediate, $C_6H_5CO\underset{A}{C}C_6H_5$, by an intermolecular oxidation–reduction rather than by the competing intramolecular oxidation–reduction (established by

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[20] Staudinger, ref. 19.

[21] The possibility that this observation may have resulted from the oxidation of free *amine*, present in the reaction mixture, seemed to be obviated by the experimental finding that the amine itself is not oxidized to the aldehyde or an addition product of the latter under the conditions used.

[22] Curtius, *Ber.*, 22,2161 (1889); J. *prakt. Chem.*, [2] 44, 182 (1891).

[23] Schroeter, *Ber.*, 42, 2336 (1909).

[24] Compare equation (4) and the discussion that follows.

the rearrangement of a phenyl nucleus) which leads to diphenylketene is the preferred course.[25]

The bearing of the results outlined in this section upon the status of the identity of triphenylacetaldehyde is of interest. Schmidlin[26] in 1910 reported that he had prepared this aldehyde by means of the action of triphenylmethylmagnesium chloride upon ethyl formate. His substance melted at 223.5° and possessed other surprising properties. The product obtained in this work from the action of mercuric oxide upon β,β,β-triphenylethylammonium nitrite was found to melt at 105° and to possess in general properties very unlike those of Schmidlin's compound. A literature search revealed that in 1917 Danilov[27] had prepared a compound having the melting point 105.5" and possessing chemical properties which left little doubt that his substance was, in fact, triphenylacetaldehyde. His preparation had been accomplished by the action of hot dilute sulfuric acid upon triphenylethylene glycol, a reaction of the pinacol–pinacolone type

$$(C_6H_5)_2C(OH)CH(OH)(C_6H_5) \longrightarrow (C_6H_5)_3CCHO + H_2O \qquad (15)$$

Our product was proved to be in all respects identical with that of Danilov and our synthesis may be said to be conclusive of the structure of the substance, since it is the first synthesis of this aldehyde from a precursor which already possesses the triphenylmethyl group.[28]

[25] Curtius and Lang [*J. prakt. Chem.*, [2] 44, 546 (1891)] observed that azibenzil is oxidized by iodine and bromine to phenylbenzoyldi-iodomethane, $C_6H_5COCI_2C_6H_5$, and phenylbenzoyldibromomethane, respectively. Staudinger, Anthes and Pfenninger, [*Ber.*, **49**, **1936** (**1916**)], have studied the action of aniline and of benzoic acid upon diphenyldiazomethane. In none of the cases in which the diazo group ($=N\equiv N$) in an aliphatic diazo compound is replaced by two halogen atoms, by oxygen or by an ionogen, H^+Y^- [for example, $H^+(HNC_6H_5)^-$; $H^+(OOCC_6H_5)^-$] is it necessary or desirable to postulate exclusively a path involving an intermediate bivalent carbon complex. Thus, if we assume for the structure of one *of* the reactive tautomers (*electromers*) of a diazo compound the electronic modification of the Thiele-Angeli structure proposed by Professor Noyes [THIS JOURNAL, 48, **2405** (1926)], $RR'\underset{\cdot\cdot}{C}:N:::N:$, it seems possible that the diazo compound may enter into reaction directly through the exposed pair $\cdot\cdot$ ("loss" to an oxidant; sharing with H+) and nitrogen be lost secondarily. In the present state of our knowledge accurate evaluation of the relative importance for a given reaction of two such alternative paths is difficult; the assumption of intermediate bivalent carbon complexes has seemed most rational for the purposes of this paper.

[26] Schmidlin, Ber., **43**, **1143** (**1910**).

[27] Danilov, *J. Russ. Phys.-Chem. Soc.*, **49**, 282 (**1917**); compare *C.* A., **19**, **1488** (**1925**).

[28] The synthesis of the aldehyde by a direct oxidation of triphenylethylamine would be slightly more determinative. Such a synthesis has actually been accomplished and will be submitted in a paper by Hellerman and Cole to THIS JOURNAL.

Danilov reported that the product of reduction of the phenylhydrazone of his aldehyde was an amine, the melting point of which was 131°. β,β,β-triphenylethylamine has since been found [Hellerman, ref. 4] to melt at 132°.

Note on the Preparation of Diphenylacetonitrile

It is desired, finally, to emphasize the utility of a simple procedure employed in the course of our experimental work involving the use of thionyl chloride as dehydrating agent in the conversion of an acid amide to the corresponding nitrile. This device has already been occasionally employed.[29] Preparation of diphenylacetonitrile in quantity by means of the methods recorded in the literature has been found to be exceedingly troublesome. It is shown here that this nitrile may be produced rapidly in good yield by the dehydration of diphenylacetamide with thionyl chloride.[30]

Experimental Part

Experiments Related to the Thermal Decomposition of **β,β,β-Triphenylethylammonium Nitrite. Preparation of the Nitrite, $(C_6H_5)_3CCH_2NH_3ONO$.**—When a small excess of a 10% solution of sodium nitrite was slowly added to a well-stirred solution of 1 g. of β,β,β-triphenylethylamine hydrochloride in 20 cc. of water, the nitrite of the amine precipitated in thin, rhomboidal plates. These were washed with ice water and dried in a vacuum desiccator over phosphorus pentoxide; decomposition point, 128°. No evidence of decomposition was found in a sample which had been stored at room temperature for several months. That the product was in fact a salt was further shown by this observation. Some of the product (which is slightly soluble in water and, of course, insoluble in ether) was shaken with a mixture of sodium hydroxide and ether; it was completely decomposed and the ether extract was found to contain free amine, while the aqueous layer retained nitrite ion.

Anal. (Dumas) Calcd. for $C_{20}H_{20}O_2N_2$: N, 8.8. Found: 8.4.

Preparation of β,β,β-Triphenylethylammonium Nitrate, $(C_6H_5)_3CCH_2NH_3ONO_2$.[31]—The nitrate, prepared in almost quantitative yield by means of the addition of an excess of 50% nitric acid to an aqueous solution of the hydrochloride, was washed with ice water and dried in a vacuum desiccator over phosphorus pentoxide; decomposition point, 239°.

Anal. (Dumas) Calcd. for $C_{20}H_{20}O_3N_2$: N, 8.4. Found: 8.2.

The Action of Heat upon the Nitrite in Aqueous Suspension. Formation of Triphenylethylene.—An aqueous suspension of the nitrite (4 g.) was heated on the steam-bath for one hour; nitrogen was evolved and the mixture became "milky." The emulsion was extracted with ether. Unchanged β,β,β-triphenylethylamine was recovered from the residual aqueous solution (after the ether extraction) by means of treatment of the latter with sodium hydroxide, extraction of the alkaline mixture with ether, evaporation of the ether, and purification of the residual solid (which was compared with an authentic sample of the amine). The ether extract of the emulsion, after being washed first with hydrochloric acid and then with water, was dried over anhydrous sodium sulfate and evaporated. A viscous oil remained, which at first resisted all attempts made to promote its crystallization; after it had been permitted to stand

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[29] (a) Hess and Dorner, *Ber.*, 50, 392 (1917); (b) Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

[30] For details see the experimental part. Hellerman and Sudzuki (unpublished work) easily prepared β,β,β-triphenylpropiononitrile from the parent amide by means of the same general method.

[31] Hellerman, THIS JOURNAL, 49, 1739 (1927)

for several weeks, it suddenly solidified when casually stirred. The crude product melted at 60–65°; it was found possible to effect purification by means of recrystallization from 90% ethanol. The pure product (1.5 g.) was found to melt constantly at 68° (corr.) and to be soluble in most of the common organic solvents. Analysis established the empirical formula, C_5H_4.

Anal. Subs., 0.2028: CO_2, 0.6970; H_2O, 0.1153. Calcd. for C_5H_4: C, 93.75; H, 6.25 Found: C, 93.73; H, 6.32.

The melting point and the empirical formula of the substance are identical with those of triphenylethylene, $(C_6H_5)_2C{=}C(H)C_6H_5$. The identity of the substance was further proved by the following. When some of it was mixed with known triphenylethylene its melting point was not depressed. Further, when some of the substance was dissolved in carbon tetrachloride, treated with bromine in excess and the product isolated by means of evaporating the solvent, the melting point of the product was found to be 90". The melting point of **α,β-dibromotriphenylethane, $(C_6H_5)_2CBrC(Br)(H)C_6H_5$**,[32] is 92°. The melting point of the product of bromination was not depressed by admixture with some of the dibroma derivative prepared from known triphenylethylene.

The Action of Heat upon the Nitrite in the Dry State.—β,β,β-Triphenylethylammonium nitrite (0.7 g.), contained in a hard glass test-tube, was heated in an oil-bath to 135° and was maintained at that temperature for half an hour. When the temperature had reached 128" (the decomposition point) a puff of nitrogen dioxide appeared and was followed by a smooth evolution of nitrogen. The cooled "melt" was shaken with ether; all dissolved except a crystalline residue which was collected and found to weigh 0.05 g. This was found to decompose at 238° and was proved to be pure β,β,β-triphenylethylammonium nitrate by means of comparison with some of the synthetic nitrate. The ethereal filtrate (from the nitrate) was saturated with dry hydrogen chloride. A solid precipitated which was collected and found to consist of 0.2 g. of the hydrochloride of β,β,β-triphenylethylamine. From the ethereal filtrate (from the hydrochloride) there was obtained, after spontaneous evaporation of the ether, a residual oil, which was proved to consist essentially of triphenylethylene, as follows. It was treated with dilute alcohol, whereupon it solidified; the solid was crystallized from 90% alcohol and was proved to be triphenylethylene, the criteria being those employed for identification of thii olefin in the preceding section.

β,β-Diphenylethylamine Hydrochloride and Sodium Nitrite

β,β-Diphenylethylamine, $(C_6H_5)_2CHCH_2NH_2$.—This amine was prepared by the method of Freund and Immerwahr,[33] which consists of the reduction by sodium of diphenylacetonitrile, $(C_6H_5)_2CH(CN)$, in alcoholic solution. The gray, pasty mass which resulted from the reduction was cautiously diluted with water, carefully neutralized with hydrochloric acid and the mixture was evaporated on a water-bath until alcohol and hydrocyanic acid were completely removed. Diphenylmethane (by-product) was removed by means of ether extraction; from the residual aqueous solution, diphenylethylamine was freed by addition of sodium hydroxide, extracted with ether and the ethereal extract treated with concentrated hydrochloric acid. The aqueous ethereal

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[32] Klages and Heilmann, *Ber.*, 37, 1455 (1904).

[33] Freund and Immerwahr, *Ber.*, 23, 2845 *(1890)*. A modification developed by Miss Sanders (Master's Dissertation, The University of Chicago, 1925) was used. The yields were quite low due to a side reaction and it is intended to investigate later the preparation of this amine by means of a method involving the rearrangement of β,β-diphenylpropionohydroxamic acid (compare reference 4). See also the method of Rupe and Gisiger [*Helv. Chim. Acta*, 8, 338 (1925)].

mixture was evaporated to dryness and the residual hydrochloride purified by means of dissolving it in the minimum quantity of anhydrous ethanol and reprecipitating with absolute ether. Its purity was indicated by its melting point (254.5') and by analysis. The yields varied (7 g. of diphenylacetonitrile gave 0.6 to 0.96 g. of amine hydrochloride).

For the preparation of diphenylacetonitrile, the initial substance, the following method involving the dehydration of diphenylacetamide with thionyl chloride has been found far superior to any of the procedures recorded in the literature, both as to ease of preparation and yield of product.

The Preparation of Diphenylacetonitrile Starting with Diphenylacetic Acid

Diphenylacetyl Chloride.[34]—Pure diphenylacetic acid,[34] 85 g. is mixed with thionyl chloride, 135 g., in a flask fitted with a ground-in condenser ("closed" with a calcium chloride tube). The mixture is heated in an oil-bath to 45° and as the reaction proceeds (sulfur dioxide and hydrogen chloride are evolved) the temperature of the bath is gradually raised to 80°; the total period of heating is five hours. The reaction mixture is next freed from most of the excess thionyl chloride by means of distillation of the latter under reduced pressure (40–45 mm.). The residue is placed in a desiccator over sodium hydroxide under a partial vacuum. After several hours, crystallization of the diphenylacetylchloride is complete. The chloride, collected and dried, is almost pure.

Diphenylacetamide.—For the next step, the preparation of diphenylacetamide, either the dried chloride in pulverized form or the crude reaction mixture containing excess thionyl chloride, obtained as detailed above after five hours' heating of diphenylacetic acid with thionyl chloride, may be used. Either of these is added in small portions to a large excess of concentrated, aqueous ammonia, which is agitated vigorously meanwhile. The resulting precipitate is collected, triturated in a mortar with aqueous ammonia and the product is again collected and finally dried at 100°. The yield of amide (based upon diphenylacetic acid taken) is practically quantitative; the "crude" product melts at 166–168° (recorded[35] m. p. 165–166°; 167.5–168°). After crystallization from alcohol the product is found to melt at 167.5–168.5°.

Diphenylacetonitrile.—Diphenylacetamide, 25 g., and thionyl chloride, 35 g., are heated together (under a return condenser protected with a calcium chloride tube) in an oil-bath (temperature of bath, 90–105") for four hours. The resulting mixture is cautiously poured upon crushed ice in order to destroy excess thionyl chloride. The suspended solid nitrile is collected, washed with water and dried in a vacuum desiccator over sodium hydroxide. The yield of crude nitrile is almost quantitative; only a small loss should occur during the process of purification, which is conducted as follows. The product is treated with a relatively large quantity of 50% ethanol and the mixture heated to not over 55°. At this point the supernatant liquid is decanted and cooled sharply. Diphenylacetonitrile crystallizes in white, glistening plates: m. p. 73.5–74°. The filtrate from these crystals or fresh 50% alcohol is used for several further extractions of residual crude nitrile under the conditions specified.

The Action of Heat upon β,β-Diphenylethylammonium Nitrite in Aqueous Solution.—β,β-Diphenylethylamine hydrochloride, 1.2 g., and sodium nitrite, 0.35 g., were dissolved in 35 cc. of water. Nothing precipitated. The solution was heated: when the temperature of the solution reached 65°, slow evolution of nitrogen began; at 75° the evolution became marked and droplets of an oil began to appear. Heating was continued at 75-80' for twenty minutes; at 90° for ten minutes; then the temperature was raised to the boiling point and the heating discontinued. As the mixture cooled the

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[34] "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. III, p. 45 (1923).

[35] Beilstein-Prager-Jacobson, Vol. IX, page 674 (1926).

oil became converted to a crystalline mass. This was collected upon a filter (leaving filtrate A, see below), washed well with water and dried on a porous plate; weight, 0.6 g. It was very soluble in alcohol. A portion washed with dilute alcohol melted at 60–68°. The product was purified by recrystallization from dilute alcohol; m. p. 67°. The physical properties of the product indicated that it was phenylbenzylcarbinol.[36] For complete characterization some of the product was boiled for twenty minutes with sulfuric acid (1:4).[16a] It was converted quantitatively to stilbene, which was identified by comparison with a sample of stilbene on hand.

Filtrate A was evaporated to dryness on the steam-bath. The residue was treated with dilute hydrochloric acid and the mixture filtered; from the filtrate by treatment with alkali, extraction with ether and treatment of the ethereal extract with hydrogen chloride, there was recovered 0.2 g. of β,β-diphenylethylamine hydrochloride. From the residual mixture of resinous and crystalline material after treatment of the first residue with acid, there was isolated a second "crop" of phenylbenzylcarbinol. No other individual could be found, although stilbene, β,β-diphenylethanol, 1,1-diphenylethylene and methyldiphenylcarbinol were sought. The latter two might have been products if rearrangements of hydrogen atoms as well as phenyl groups had taken place.[37]

The Action of Heat upon a Mixture of β,β-Diphenylethylamine Hydrochloride and Sodium Nitrite in Equimolecular Proportion.—An intimate mixture of diphenylethylamine hydrochloride, 0.34 g., and sodium nitrite, 0.12 g. (1 mole), contained in a hard glass test-tube was heated in a glycerine-bath; at 160° there was a slight evolution of a gas and droplets of an oil began to collect upon the walls of the tube above the mixture. At 195° the mass had become yellowish-brown in color; the heating was continued at 195° until forty minutes had elapsed after the temperature had reached 160°. The cooled reaction product was extracted with ether. A white solid consisting largely of sodium chloride remained. The ethereal extract was treated with dry hydrogen chloride and filtered from a slight quantity of amine hydrochloride. The filtrate from the hydrochloride was allowed to evaporate. The residue, which consisted of crystals embedded in viscous liquid, was washed with water and then treated with cold alcohol, whereupon white needles separated. These were recrystallized from ether and were found to melt at 124.5'. The melting point of a mixture of the product with known stilbene (recorded m. p. 125°) was also 124.5°. The yield was 0.2 g. (76%).

β,β-Diphenyldiazo-ethane

The Preparation of β,β-Diphenylethyl Urethan, $(C_6H_5)_2CHCH_2NHCOOC_2H_5$.—When 1.9 g. of β,β-diphenylethylamine hydrochloride was shaken violently with 1.5 g. of ethyl chlorocarbonate and an excess of 25% sodium carbonate, β,β-diphenylethylurethan separated as a white, crystalline solid. This was collected, washed with water and dried over sulfuric acid. The melting point, 69–70', was not raised when the substance was crystallized from ligroin;[38] yield, 93%.

Anal. (Dumas) Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: 5.21.

The Preparation of β,β-Diphenylethylnitroso-urethan, $(C_6H_5)_2CHCH_2N(NO)$-$COOC_2H_5$.—After considerable experimentation, there was devised the following procedure which, carefully followed, leads to high yields of the nitroso compound.

Of thoroughly dried β,β-diphenylethylurethan, 1 g. was dissolved in 30 cc. of anhydrous ether, anhydrous sodium sulfate, about 3 g., was added, and the mixture,

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[36] Ref. 35, Vol. VI, p. 683.

[37] See the theoretical section.

[38] Sieglitz, Ber., 55, 2040 (1922), prepared the same compound by means of the rearrangement of β,β-diphenylpropionoazide in alcoholic solution.

contained in a flask, suitably protected from moisture with a calcium chloride tube, was cooled in an ice-salt bath. The gases prepared by treatment of sodium nitrite with 80% sulfuric acid and dried by calcium chloride were introduced into the ethereal mixture until the latter had assumed a dark green hue. The sodium sulfate was removed by filtration; the filtrate was placed over sulfuric acid in a desiccator connected to a suction pump and ether was allowed to evaporate at room temperature. The product was a stable, viscous, straw-colored oil; it exhibited chemical properties which are common to N-nitroso compounds. The yield was practically quantitative.

Anal. (Dumas) Calcd. for $C_{17}H_{18}N_2O_3$: N, 9.39. Found: 9.13.

β,β-Diphenyldiazo-ethane, $(C_6H_5)_2CHCH(N_2)$.[39]—β,β-Diphenylethylnitroso-urethan, 0.235 g., dissolved in 2 cc. of anhydrous ether (contained in a flask suitably protected from moisture) was placed in a freezing mixture at −15°. To this solution was added 0.5 cc. of absolute ethanol in which had been "dissolved" 0.025 g. of sodium. The resulting solution was permitted to remain below −10° for three hours, during which it assumed a red color which deepened progressively. The flask was quickly transferred to a vacuum desiccator which was surrounded with ice-salt mixture and which was connected with a suction pump through a line suitably protected from moisture. In this manner the solvents were evaporated at −10° to −15°. A red, semi-crystalline mass remained. An assay of this product for *diazo* nitrogen indicated that *well over* 80% of the nitroso-urethan taken had been converted to β,β-diphenyldiazo-ethane. That this diazo compound was, in fact, present was proved further by its properties (see below), particularly its conversion when heated in aqueous suspension to the dihydrazone (azine) of diphenylacetaldehyde, $[(C_6H_5)_2CHCH{=}N]_2$. Time was not taken to effect complete purification of the compound; this could probably be effected by means of crystallization from an appropriate solvent at low temperatures (below −10°). The diazo compound was successfully prepared several times (in up to 1 g. portions) by means of the procedure here outlined.

Decomposition of the Diazo Compound

(A) Spontaneously.—While the diazo compound, as prepared above, may be kept below −10° for many hours, it begins to evolve nitrogen when the temperature is permitted to rise to 0°. A sample allowed to remain above 0° for twelve hours was found to have resolved itself into a yellow resinous mass which contained no diazo nitrogen and which yielded no definite chemical individual after treatment with various solvents.

(B) When Heated in Acid Environment: **Stilbene.**—β,β-Diphenyldiazo-ethane, prepared from 0.23 g. of β,β-diphenylethylnitroso-urethan, was gradually heated with dilute sulfuric acid (1 part acid: 4 parts water) almost to the boiling point of the acid until evolution of nitrogen had ceased. The mixture was cooled and the reddish-yellow oil which had formed was extracted with ether and recovered by means of evaporation of the solvent. The viscous residue (0.18 g.) was treated with 95% alcohol, whereupon a nearly white solid separated. The latter was washed with alcohol, collected and crystallized from ether; m. p. 122°. It was proved to be stilbene by means of comparison with an authentic sample of stilbene. It was further characterized by conversion to long, yellow needles of stilbene picryl chloride (m. p. 71°) according to the procedure of Liebermann and Palm.[40]

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[39] Our method of preparation of the compound is, of course, a modification of Von Pechmann's general procedure [*Ber.*, 27, 1888 (1894)] for the preparation of aliphatic diazo compounds. Compare Oppé, *Ber.*, 46, 1095 (1913).

[40] Liebermann and Palm, *Ber.*, 8, 378 (1875).

(C) When Heated in Alkaline and in Neutral Environment: **Diphenylacetaldazine,** $(C_6H_5)_2CHCH{=}NN{=}CHCH(C_6H_5)_2$.—Some of the diazo compound which had been washed with cold water was mixed with water and heated on the steam-bath until evolution of nitrogen had ceased. After several hours the water was decanted from the reddish-yellow, oily product and the latter was treated with ether. A white powder, insoluble in the ether, remained. This was repeatedly treated with boiling ether until it melted constantly at 165°. The recorded melting point of diphenylacetaldazine (prepared by treatment of diphenylacetaldehyde with hydrazine hydrate) is 165°.[41]

Anal. (Dumas) Calcd. for $C_{28}H_{24}N_2$: N, 7.41. Found: 7.60.

When some β,β-diphenyldiazo-ethane in the dry state was subjected to the action of heat, the aldazine was likewise found to be a product. The same product was obtained after some of the diam compound was decomposed on the steam-bath in the presence of concentrated aqueous ammonia. No other definite compound was isolated from these various reaction mixtures.

The study of the decomposition products of β,β-diphenyldiazo-ethane and similar compounds is being continued (by L. H. and R. E. H.).

Triphenylacetaldehyde from the Action of Mercuric Oxide upon β,β,β-Triphenylethylammonium Nitrite

An intimate mixture of the nitrite (1 g.) and yellow mercuric oxide, freshly precipitated and dried over phosphorus pentoxide (5 g.), was heated for half an hour at 135°. The reaction mixture was extracted with ether. The ethereal extract, treated with dried hydrogen chloride, yielded about 0.1 g. of β,β,β-triphenylethylamine hydrochloride. The filtrate from the hydrochloride was allowed to evaporate spontaneously. The residue consisted largely of triphenylethylene in a semi-crystalline deposit on the bottom of the beaker. On the upper sides of the beaker rhomboidal plates had collected. Several of these were removed and washed with a small portion of cold 90% alcohol; m. p. 104°. The contents of the beaker were extracted with ligroin (b. p. 30–60°); the ligroin extract after evaporation of the solvent yielded well-defined plates which were recrystallized from ligroin and found to melt at 104–105°. When they were mixed with some known triphenylacetaldehyde[27] (m. p. 105°) the melting point was not depressed.

Triphenylacetaldehyde is not formed when triphenylethylamine is substituted for its nitrite in the above experiment.[42]

Benzil from the Action of Mercuric Oxide upon Azibenzil[43]

Azibenzil (phenylbenmyldiazomethane), $C_6H_5COC(N_2)C_6H_5$, was prepared in excellent yield from benzil monohydrazone by the method of Curtius and Thun.[44] An intimate mixture of the pure diazo compound, 1 g., and moist mercuric oxide (freshly precipitated and well washed), 20 g., contained in a large test-tube, was heated in a

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[41] Klages and Kessler, Ber., 39, 1756 (1906).

[42] Hellerman and Cole, unpublished work, An extended investigation of the behavior of nitrites and other salts of amines with oxides of heavy metals is in progress. A preliminary experiment has indicated that the action of mercuric oxide upon β,β-diphenylethylammonium nitrite yields diphenylacetaldehyde in addition to rearrangement products.

[43] We are indebted to Mr. J. R. Sudzuki who aided with the experimental work outlined under this caption.

[44] Curtius and Thun, J. prakt. Chem., [2] 44, 182 (1891).

glycerine bath to 100°. The mixture became gray due to separation of mercury. The reaction mixture was extracted with absolute alcohol. From the alcoholic extract there was obtained, after evaporation of the solvent in a stream of air (without heat), 0.7 g. of light yellow crystals of almost pure benzil. The product, recrystallized several times from alcohol, was identified by its melting point and by comparison with an authentic sample of benzil. It was further characterized by conversion to the monohydrazone, which was compared with a sample of benzil monohydrazone on hand.

Summary

1. The nitrite and nitrate of β,β,β-triphenylethylamine have been prepared and described. They are stable, solid substances at room temperature. The nitrite is one of the few nitrites of amines of Type RCH_2NH_2 which have been isolated.

2. The principal product of the action of heat upon the nitrite in aqueous suspension has been shown to be triphenylethylene. It has been shown further that the nitrite, heated in the dry state, yields also β,β,β-triphenylethylammonium nitrate.

3. An hypothesis to account for the product of thermal decomposition and to interpret the action by which it is produced has been developed. This hypothesis, which involves diazotization of the amine and subsequent formation of a transitorily existing methylene intermediate, has been found to be useful in the interpretation of various amine nitrite decompositions which have been recorded in the literature.

4. The thermal decomposition of the nitrite of β,β-diphenylethylamine has been shown to lead to phenylbenzylcarbinol or to stilbene, depending upon the conditions.

5. β,β-Diphenyldiazo-ethane has been prepared (in a somewhat impure state) and its behavior under various conditions studied. Its behavior, when heated under certain conditions, is interestingly related to the thermal behavior of β,β-diphenylethylammonium nitrite.

6. It has been shown that the action of mercuric oxide upon β,β,β-triphenylethylammonium nitrite at 135° results in the formation of triphenylacetaldehyde in addition to triphenylethylene. This is the first observation of the formation of triphenylacetaldehyde from a precursor which possesses the triphenylmethyl group.

7. It has been shown that azibenzil, heated with moist mercuric oxide, undergoes to no large extent the Schroeter rearrangement to diphenylketene, but instead gives benzil in 74% yield.

8. Improved methods for the preparation of diphenylacetamide and diphenylacetonitrile are submitted.

9. The preparation of β,β-diphenylethylnitroso-urethan, starting compound for β,β-diphenyldiazo-ethane, is described. An improved method is outlined for the preparation of the parent urethan.

BALTIMORE, MARYLAND

[CONTRIBUTIONPROM THE BAKER LABORATORY Of CHEMISTRY, CORNELL UNIVERSITY]

HYDROQUINOLSULFONEPHTHALEIN AND SOME OF ITS DERIVATIVES

BY W. R. ORNDORFF AND C. V. SHAPIRO[1]

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The preparation of hydroquinolsulfonephthalein was first attempted by Sohon[2] but it is questionable whether he actually isolated it, as his description of its properties accords, not with that of the pure compound which has now been obtained in a crystalline state, but rather with that of an amorphous by-product whose constitution has not been established.

Hydroquinolsulfonephthalein is the sulfonic acid analog of hydroquinolphthalein. The constitution of the salts of the latter compound has been the subject of considerable debate,[3] due to the fact that it does not lend itself to normal para- or ortho-quinoid formulation. Two configurations, the meta-quinoid of Meyer[aa] and the ortho-quinoid of Green,[3b] have received the most attention, but both are subject to criticism, the former from stereochemical considerations and on account of its uniqueness, since no other admittedly meta-quinoid compound is as yet known. Green's formula, on the other hand, does not account for all of the chemical properties of hydroquinolphthalein. A study of the chemical properties of hydroquinolsulfonephthalein and of the absorption spectra of these **two** compounds has led us to regard the meta-quinoid constitution as representing their behavior most consistently. Hydroquinolsulfonephthalein is quinoid in the free state and exists as an inner salt, since it does not form a hydrochloride, either in solution or in the solid state when exposed to hydrogen chloride. The basic properties of the phthaleins are assumed to reside in the quinoid oxygen and in the present instance it **is** neutralized by the sulfonic acid group. On the other hand, hydroquinolphthalein reacts with hydrogen chloride to form a colored salt and, as will be shown later, the absorption spectrum of this salt is identical in its general features with that of a neutral solution of hydroquinolsulfonephthalein. These facts cannot be accounted for either by the ortho-quinoid structure or by any other configuration which simultaneously

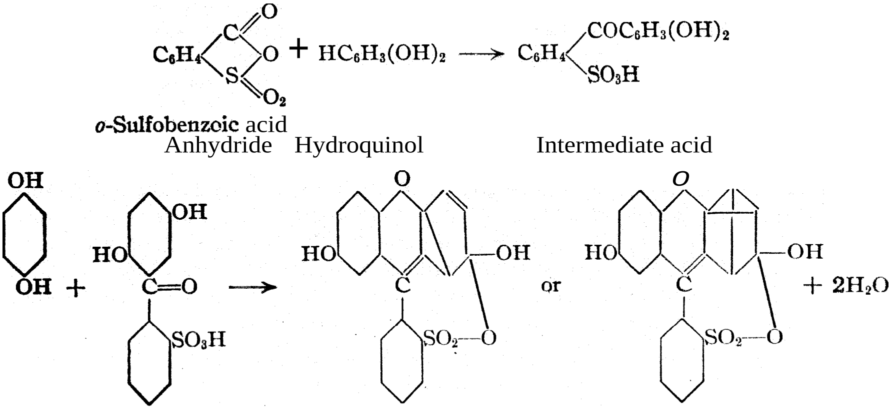
[1] This article is based on a portion of a thesis submitted to the Faculty of the Graduate School of Cornell University by C. V. Shapiro in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Sohon, *Am. Chem.* J., *20,257* (1898).

[3] (a) Meyer and co-workers, *Ber.*, 36, 2949 (1903); 38, 1318, 3958 (1905); 40, 1437 (1907); 41, 2437 (1908); 42, 2814 (1909); 44, 1954 (1911). (b) Green and co-workers, J. *Chem. Soc.*, 85, 398 (1904); *Ber.*, 39, 2365 (1906); 40, 3724 (1907); *Proc. Ckm. Soc.*, 24, 206 (1908); J. *Soc. Chem. Ind.*, 27, *4* (1908). (c) Baeyer, *Ann.*, 372, 80 (1910); *Ber.*, 46, 70 (1913). (d) Kehrmann, *Ann.*, 372, 287 (1910). *(e)* H. Liebig, *J. prakt. Chem.*, 85, 97 (1912). (f) Dominikiewicz, *Roczniki Chem.*, 3, 350 (1923); *J. Chem. Soc. Abstracts*, 128, 53 (1925).

satisfies the condition that only dibasic and not tri- or tetrabasic metallic salts can be obtained from either of these phthaleins.

By analogy with the other phthaleins and sulfonephthaleins which have been studied in this Laboratory, it is probable that the formation of hydroquinolsulfonephthalein occurs in two steps, although no success attended efforts to isolate the intermediate acid.



Hydroquinolsulfonephthalein

Hydroquinolsulfonephthalein, as indicated above, contains the pyrone ring and analysis shows it to have the empirical formula $C_{19}H_{12}O_6S$, not $C_{19}H_{14}O_7S$ as suggested by Sohon.[4] It is, therefore, isomeric with sulfonefluoresceins but unlike that compound shows no trace of fluorescence in alkaline solution. Hydroquinolphthalein bears a similar relation in structure and fluorescence properties to fluorescein.

Hydroquinolsulfonephthalein does not appear to behave as a tautomeric compound, since no colorless, lactoid derivatives could be obtained from it. It forms a cream-colored dibenzoate which yields a bright yellow alcoholic solution. The absorption spectrum of this solution confirms the quinoid nature of this compound, since it fails to show certain bands the presence of which has served as an excellent criterion for benzenoid derivatives of the triphenylmethane series.[6]

Experimental Part[7]

Preparation of Hydroquinolsulfonephthalein. 1. From the Anhydride of o-Sulfobenzoic Acid and Hydroquinol.—Fifty g. each of hydroquinol and of the anhydride of o-sulfobenzoicacid were heated together at 150°, but as soon as the mixture had be-

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[*] Ref. 2. Evidently due to a typographical error, this formula is given in Sohon's article as $C_{19}H_{14}O_8S$.

[5] Orndorff and Vose, THIS JOURNAL, **46, 1896 (1924).**

[6] Gibbs and Shapiro, Proc. *Nat.* Acad. *Sci.,* **14, 251 (1928).**

[7] We are indebted to the Monsanto Chemical Works of St. Louis for the saccharin used in this investigation.

come fluid the temperature was quickly lowered to 130". The fusion was continued for eighteen to twenty-four hours, although even after longer periods of heating the mixture did not become hard. An air condenser was provided for the flask to avoid loss of hydroquinol by sublimation; the crystals of hydroquinol were occasionally pushed down and the mixture stirred. At the end of the condensation 200 cc. of water was added to the hot melt, the solution was allowed to stand for several hours and the hydroquinolsulfonephthalein was filtered off. The precipitate was washed with small portions of distilled water to remove excess mother liquor, but large volumes of water must be avoided in handling the crude sulfonephthalein as the impure material is fairly soluble. The washed sulfonephthalein was dissolved in 100 cc. of 5% sodium bicarbonate solution by boiling, the solution filtered, diluted with one liter of distilled water and again brought to a boil. Small amounts of 5% hydrochloric acid were added and the liberated tarry matter was filtered off as it appeared until neutralization was effected, when the hydroquinolsulfonephthalein separated in small, dark brown crystals. An alternative method for the preliminary purification was to suspend the dried, crude sulfonephthalein in 100 cc. of cold, absolute alcohol for one hour with frequent stirring, filter and wash with several 10 cc. portions of alcohol. Further purification was necessary in both cases by one or two reprecipitations from a boiling bicarbonate solution, after which the compound was obtained in the form of shining red plates. The average yield was 20%. The material was dried at 110° prior to analysis.

Anal. Subs. (dry), 0.3025, 0.4930: $BaSO_4$, 0.1945, 0.3152. Calcd. for $C_{19}H_{12}O_6S$: S, 8.71. Found: 8.83, 8.78. Calcd. for $C_{19}H_{14}O_7S$: S, 8.29.

2. From the Anhydride of *o*-Sulfobenzoic Acid and Hydroquinol in the Presence of Dehydrating Agents.—Numerous attempts were made to improve the yield and quality of hydroquinolsulfonephthalein by carrying out the condensations in the presence of dehydrating agents such as zinc chloride, sulfuric acid, boric acid and stannous chloride. With the exception of the first mentioned compound, excessive tar formation occurred which rendered the purification a prolonged and difficult process. With zinc chloride the best yield obtained was 5% with very little tarry contamination, but when a higher temperature or more prolonged heating was employed to raise the yield, the production of tar again increased.

A condensation of saccharin with hydroquinol in the presence of concd. sulfuric acid resulted in the recovery of a small amount of amorphous material which dissolved in alkali with a yellow-brown color, recalling Sohon's description[5] of the behavior of the substance he thought to be hydroquinolsulfonephthalein. As the material could not be obtained in a crystalline state no attempt was made to analyze it.

Properties of Hydroquinolsulfonephthalein.—Hydroquinolsulfonephthalein crystallizes from a hot, aqueous solution, slightly acidified with hydrochloric acid, in the form of dark red, thin plates which grind up to a bright red powder. It is practically insoluble in most organic solvents. In methyl and ethyl alcohol and in water it dissolves sparingly to give an orange-red solution, but the solubility is greatly increased by the presence of traces of impurity. An exact solubility determination for a highly purified sample yielded 0.0117 g. per 100 cc. at 22° in distilled water and 0.0120 g. per 100 cc. in absolute ethyl alcohol. Sodium hydroxide solutions dissolve it readily, sodium carbonate more slowly, to give a deep blue-purple solution. The color of both solutions changes very rapidly to a tan or brown. A 5% solution of sodium bicarbonate dissolves it slowly, even at the boiling point, but the solution is relatively stable as no change of the purple color was observed after standing for several days.

Dr. Barnett Cohen of the Hygienic Laboratory, U. S. Public Health Service, Washington, D. C., has kindly determined the indicator properties of hydroquinolphthalein and hydroquinolsulfonephthalein and an excerpt from his report follows.

"**Hydroquinolphthalein.**—This beautifully crystallized compound dissolved readily in alcohol and behaved very much like phenolphthalein, except that the color range lies between P_H 8.6 and P_H 10.

"**Hydroquinolsulfonephthalein.**—When tested in buffers of different P_H, the indicator gave a brownish-yellow coloration from P_H 1 down to P_H 5. Between P_H 5.0 and 6.0 the color became a purer yellow. Between P_H 6.4 and 8.0 there was a definite stepwise change in coloration from yellow through greenish-yellow to dark olive. At P_H 8.0 the color was dark olive with a violet tinge. From P_H 8 to 10 there was also a definite stepwise color change to deeper shades of purple. Apparently there are two dissociations which overlap near P_H 8. From my preliminary measurements, I should say that one dissociation constant is at P_K 7.2 and the other at 8.8."

Hydroquinolsulfonephthalein does not melt below 300°. It dissolves in concentrated sulfuric acid, forming an orange solution, and is partially precipitated when the solution is poured into a large volume of water. It does not absorb hydrogen chloride when exposed to the dry gas, which indicates that it possesses an inner salt structure. This agrees with the subsequent observation, in a study of the absorption spectra of hydroquinolsulfonephthalein, that the addition of dry hydrogen chloride gas to an alcoholic solution produces no change in its absorption, even in ratios as high as 10,000 molecules of acid to one of the sulfonephthalein.

Action of Ammonia Gas.—When dry hydroquinolsulfonephthalein was exposed to ammonia gas, previously dried over sodium, it absorbed about three molecules of ammonia and became blue-black in color.

Anal. Subs., 0.1076; gain, 0.0125. Calcd. for $C_{19}H_{12}O_6S + 3NH_3$: NH_3, 12.19. Found: 10.39.

When allowed to stand in a desiccator over concentrated sulfuric acid until it reached constant weight, the sample retained one molecule of ammonia.

Anal. Subs., 0.1076; gain, 0.0050. Calcd. for $C_{19}H_{12}O_6S + NH_3$: NH_3, 4.41. Found: 4.44.

The mono-ammonium salt dissolves in water with a murky green color; this is due to hydrolysis, since the true color of the salt is blue-purple and that of the neutral sulfonephthalein, orange-red. A similar effect has been obtained in the study of the absorption spectra of alkaline solutions of hydroquinolsulfonephthalein, where even with four molecules of potassium hydroxide to one of the sulfonephthalein it is found that the characteristic bands of the neutral substance and its salt are simultaneously present.

Salts of Hydroquinolsulfonephthalein.—The disodium salt of hydroquinolsulfonephthalein was obtained by treating the latter with an alcoholic solution of sodium ethoxide. The air dried product contained a molecule of alcohol of crystallization ($C_{19}H_{10}O_6SNa_2 + C_2H_5OH$).

The barium salt ($(C_{19}H_{11}O_6S)_2Ba$) was obtained by boiling a suspension of hydroquinolsulfonephthalein and barium hydroxide in water, filtering and concentrating. After several recrystallizations from water it was separated entirely free from barium hydroxide in the form of brown, flaky plates.

Hydroquinolsulfonephthalein Dibenzoate.—Three g. of hydroquinolsulfonephthalein was boiled with 100 cc. of benzoyl chloride for one hour. The solution was filtered and the excess benzoyl chloride evaporated off in a water oven. The residue was extracted several times with warm benzene to remove tarry matter, after which it was dissolved in boiling benzene and recrystallized from that solvent several times. Two g. of pale, cream-colored crystals was obtained, but when heated at 110° to remove benzene they changed to a bright yellow color.

Anal. Subs. (dry), 0.2098, 0.3551: $BaSO_4$, 0.0844, 0.1411. Calcd. for $C_{19}H_{10}O_6S(C_6H_5CO)_2$: S, 5.56. Found: 5.53, 5.46.

The maximum solubility of the dibenzoate in absolute ethanol was determined at 22° as 0.0150 g. per 100 cc. It is also very difficultly soluble in methanol, benzene, toluene and acetone. It is slowly saponified by boiling with dilute sodium hydroxide solution, when the characteristic blue color of the sulfonephthalein in alkaline solution appears.

Summary

1. The preparation of pure, crystalline hydroquinolsulfonephthalein has been described. It gives evidence of being an inner salt and on the basis of its chemical and physical behavior it is accorded a meta-quinoid structure.

2. Hydroquinolsulfonephthalein gives colored metallic salts and a colored dibenzoate, but unlike the other phthaleins and sulfonephthaleins, it does not yield any colorless, lactoid derivatives.

ITHACA, NEW YORK

[CONTRIBUTION FROM RESEARCH LABORATORIES, GOODYEAR TIRE AND RUBBER COMPANY]

ACTION OF NASCENT THIOCYANOGEN UPON ISOPRENE AND DIMETHYLBUTADIENE

BY HERMAN A. BRUSON AND WILLIAM A. CALVERT

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The identification of certain low boiling, unsaturated hydrocarbons which yield only liquid addition products with the halogens or hydrogen halides is often a matter of considerable difficulty. Especially is this true of isoprene which readily undergoes substitution, polymerization and resinification upon treatment with bromine or hydrogen bromide. By the use of hypochlorous or hypobromous acids Mokijewski[1] obtained crystalline addition compounds of isoprene which serve as characteristic derivatives.

In attempting to prepare a derivative which would be more stable it occurred to us to treat both isoprene and its methyl homolog, 2,3-dimethylbutadiene, with thiocyanogen. Soderback[2] and Kaufmann[3] as well as Challenger and others[4] have observed that thiocyanogen adds to the unsaturated bonds of organic compounds in a manner analogous to bromine and forms, in many cases, well defined, crystalline addition products. However, no mention is made concerning the action of thiocyanogen upon unsaturated hydrocarbons containing two reactive double bonds as exemplified by the butadienes.

When a solution of thiocyanogen prepared by the method of Söderbäck[2] from lead thiocyanate and bromine in anhydrous benzene, was allowed to react in excess at 0° with either isoprene or 2,3-dimethylbutadiene, addition took place, but only traces of crystalline reaction products could be isolated. Polymerization of the thiocyanogen to the insoluble compound (SCN), apparently occurred before any appreciable addition to the hydrocarbon was effected.

However, by generating the thiocyanogen in the nascent state according to the method of Kaufmann and Oehring[5] addition took place smoothly at 5°, isoprene and dimethylbutadiene yielding beautiful, crystalline compounds of sharp melting point. The analysis of these addition products indicated that only one mole of $(SCN)_2$ added to one mole of hydrocarbon despite the fact that a slight excess of thiocyanogen was available for completely adding to both double bonds. No tetrathiocyanate could be isolated under the conditions employed.

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[1] Mokijewski, *Chem. Z.*, 19, 2254; *Chem. Zent.*, 70, *I*, 590 (1899).

[2] Söderbäck, *Ann.*, 419,217 (1919); 443, 142 (1925).

[3] Kaufmann, *Ber. deut. pharm. Ges.*, 33, 139 (1923).

[4] Challenger, Smith and Paton, J. *Chem. Soc.*, 123, 1046 (1923); Challenger and Bott, *ibid.*, 127,1039 (1925).

[5] Kaufmann and Oehring, *Ber.*, 59, 187 (1926).

We have not investigated the mode of addition, that is, whether it is 1,2 or 1,4. The behavior of butadiene[6] and of isoprene[7] with bromine and hydrogen bromide would indicate that the addition of $(SCN)_2$ would by analogy also occur preferentially in the **1,4-position,** although in view of the recent work of Farmer, Lawrence and Thorpe[8] some doubt is cast upon the infallibility of **1,4-addition** in the case of butadiene.

The addition product of thiocyanogen with isoprene and with dimethylbutadiene is a useful, characteristic derivative for purposes of identification and for further synthetic work.

Experimental

Isoprene and $(SCN)_2$.—The isoprene was prepared by passing the vapors of limonene over a glowing platinum spiral in *vacuo.*[9] The crude isoprene (b. p. **33-40**") thus obtained was allowed to stand over barium peroxide for ten days to remove amylenes and was then fractionated using a three-foot Vigreaux column with baffles. The fraction boiling at **33–34**" was used.

Ten cc. of isoprene (**7** g.) dissolved **in 35** cc. of glacial acetic acid was added to a solution of **36** g. of sodium thiocyanate dissolved in **335 cc.** of glacial acetic acid, and into the cooled mixture at 5–6° a solution of **11 cc.** of bromine dissolved in **65 cc.** of glacial acetic acid was slowly allowed to drop, the thiocyanate solution meanwhile being vigorously stirred. The room was darkened so that a minimum of polymerization of the thiocyanogen would occur.

After addition **of** the bromine solution, which should take about fifteen minutes, the stoppered mixture was allowed to stand in the ice chest for twelve hours. The yellow precipitate of polymerized thiocyanogen was filtered **off** and washed with 50 cc. of glacial acetic acid, the washings being combined with the filtrate, which was then diluted with twice its volume of water and made alkaline by the addition of excess solid sodium carbonate. A yellowish, waxy material separated. It was skimmed off, washed with cold water, then dissolved in **50** cc. of cold benzene and filtered. The filtrate when added to 100 cc. of cold ligroin and stirred crystallized in glistening plates. The slightly yellowish crystals were purified by bone-blacking once in hot benzene and recrystallizing twice from benzene–ligroin mixture; yield of pure product, 4 g.

The pure dithiocyano addition product of isoprene formed colorless, glistening platelets, m. p. **76–77'** (corr.). It is very soluble in cold benzene, chloroform, acetone, ether and alcohol, somewhat less soluble in glacial acetic acid and only slightly soluble in petroleum ether or cold ligroin. For analysis the compound was dried in high vacuum at 35°.

Anal. Subs., **0.2166** required **23.5** cc. of **0.1** N H_2SO_4 (Kjeldahl); **0.1240** gave **0.3166** g. of $BaSO_4$ (Carius). Calcd. for $C_7H_8S_2N_2$: S, **34.77;** N, **15.21.** Found: S, **35.00; N, 15.19.**

Mol. wt. (Cryoscopic in benzene; $K = 51$). Subs., **0.1052, 0.1976;** benzene, **16.16.** ΔT, 0.182°, 0.335°. Calcd.; **184.** Found: 182.4, 186.4.

The compound possesses a faint, disagreeable odor; its solutions cause blistering of the skin and its dust creates a sickening metallic taste in the mouth when inhaled.

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[6] Thiele, ***Ann.,*** 308, **339 (1899).**

[7] Staudinger and others, ***Helv. chim. acta,*** **5, 743, 756 (1922).**

[8] Farmer, Lawrence and Thorpe, *J. Soc. Chem. Ind., 47* **[4] 101 (1928).**

[9] Staudinger and Klever, Ber., 44, **2215 (1911).**

Dimethylbutadiene and $(SCN)_2$

The 2,3-dimethylbutadiene was prepared by the catalytic dehydration of anhydrous pinacone, according to the method of Kyriakides[10] employing hydrobromic acid. After purification and fractionation, it boiled at 67–60°.

Twenty cc. (15 g.) of dimethylbutadiene dissolved in 75 cc. of glacial acetic acid was added to 500 cc. of glacial acetic acid containing 72 g. of dissolved potassium thiocyanate, and into the cooled mixture at 6° a solution of 18.6 cc. of bromine in 110 cc. of glacial acetic acid was allowed to drop slowly with stirring. After standing for twelve hours in the ice chest, the precipitate was filtered off and washed with water to remove acetic acid and inorganic salts. It was dried by washing with alcohol and ether, then boiled with 100 cc. of benzene and filtered hot through a hot water funnel. The yellow, insoluble $(SCN)_x$ remains behind on the filter. The filtrate upon cooling crystallized in yellowish needles which were bone-blacked in boiling benzene and allowed to recrystallize. For analysis the compound was redissolved in boiling ethyl acetate and upon cooling crystallized in well formed, colorless, odorless, rhombohedrons; yield, 5 g. of pure product; m. p. 130° (corr.).

It is very difficultly soluble in boiling alcohol, ether or acetone, but dissolves in hot benzene, chloroform and ethyl acetate. It was dried in a high vacuum at 75° for analysis.

Anal. Subs., 0.1290 required 13.3 cc. of 0.1 *N* H_2SO_4 (Kjeldahl); 0.1342 gave 0.3159 g. of $BaSO_4$ (Carius). Calcd. for $C_8H_{10}S_2N_2$: S, 32.31; N, 14.14. Found: S, 32.27; N, 14.43.

Summary

Isoprene and dimethylbutadiene each add one molecule of thiocyanogen to form well defined, crystalline addition products which may be used to characterize these hydtocarbons.

AKRON, OHIO

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

HEXA-TERTIARY-BUTYLETHYNYLETHANE

BY PAUL L. SALZBERG WITH C. S. MARVEL

RECEIVED MARCH 1, 1928 PUBLISHED JUNE 5, 1928

The observed cases of dissociation of hexa-substituted ethanes have been limited to compounds containing at least two aryl groups attached to each of the carbon atoms which tend to separate and become trivalent. Consequently it has seemed logical to attribute the weak character of the ethane linkage to some properties of the neighboring aromatic nuclei, such as size (steric hindrance), weight and degree of unsaturation.

It has been suggested several times that the substitution of unsaturated aliphatic radicals for the hydrogen atoms of ethane might also weaken the central carbon–carbon bond. An indication of the similarity between the unsaturation of an acetylenic linkage and of a benzene nucleus has

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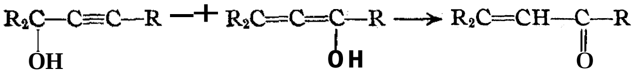
[10] Kyriakides, THIS JOURNAL, 36, 991 (1914).

been obtained by Hess and Weltzien,[1] who has shown that phenylethynyldiphenylcarbinol, diphenylethynylphenylcarbinol and triphenylethynylcarbinol exhibit the halochromic properties which are characteristic of triphenylcarbinol. However, more recently Moureu, Dufraisse and Houghton[2] have prepared diphenylethynyltetraphenylethane and found that it does not absorb oxygen on heating but instead rearranges to an isomeric hydrocarbon. In this Laboratory, Gray and Marvel[3] have pointed out that the unsaturation present in three triple bonds might be comparable to that in two phenyl radicals, since in both cases there are twelve more electrons shared between carbons than would be the case in the corresponding saturated compounds. The molecular weight of the *tert.*-butylethynyl radical (81) is comparable to that of the phenyl radical (77) and there should be less possibility of steric hindrance with this compact acetylenic radical than with any other arrangement of six carbons with the required amount of unsaturation. Accordingly an attempt was made to prepare hexa-*tert.*-butylethynylethane. No definite results were obtained in that work.

In the present investigation crystalline hexa-*tert.*-butylethynylethane has been prepared from tri-*tert.*-butylethynylcarbinol as the starting material. This carbinol was prepared by addition of ethyl chlorocarbonate to *tert.*-butylethynylmagnesium bromide which was found to give better yields than sodium *tert.*-butylacetylide. The carbinol exhibited several of the characteristic halochromic properties of triphenylcarbinol. An ether solution became yellow on the addition of perchloric acid, dark red on the addition of concentrated sulfuric acid and formed a crystalline addition compound with stannic chloride. An attempt was made to dissolve the carbinol in a concentrated hydrochloric acid solution of zinc chloride in order to try the reduction to the ethane by means of vanadous chloride,[4] but this was unsuccessful.

The above tests carried out in the presence of strong mineral acids are complicated by the tendency of acetylenic carbinols to undergo a characteristic rearrangement to give α,β-unsaturated ketones, which may themselves exhibit halochromic properties. This rearrangement has been studied by Meyer and Schuster[6] for several phenylethynylcarbinols and they have shown that the reaction involves the migration of the hydroxyl group to the beta carbon atom and subsequent ketonization of the enol thus formed.



$$\underset{\text{OH}}{\underset{|}{R_2C}}-C\equiv C-R \longrightarrow R_2C=C=\underset{\text{OH}}{\underset{|}{C}}-R \longrightarrow R_2C=CH-\underset{\text{O}}{\underset{\|}{C}}-R$$

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[1] Hess and Weltzien, *Ber.*, 54, 2511 (1921).

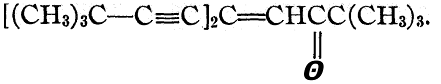
[2] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] 41, 56 (1927).

[3] Gray and Marvel, THIS JOURNAL, 47, 2796 (1925).

[4] Conant and Sloan, *ibid.*, 45, 2466 (1923); 47, 572 (1925).

[5] Meyer and Schuster, *Ber.*, 55, 819 (1922).

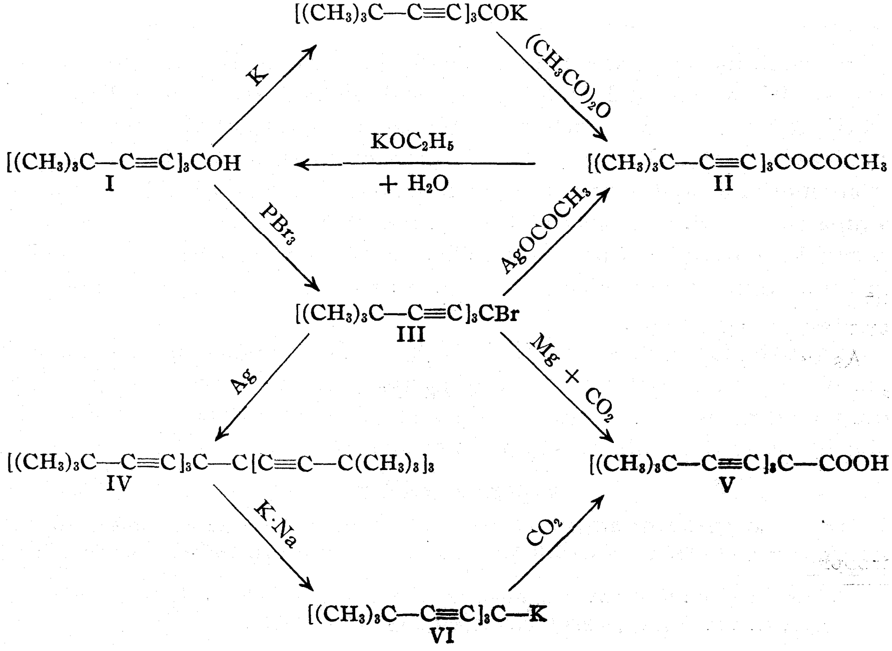
When tri-*tert.*-butylethynylcarbinol was treated with concentrated sulfuric acid under the conditions described for the rearrangement of phenylethynyldiphenylcarbinol, there was obtained a yellow product, isomeric with the original carbinol, which has been assigned the structure



$$[(CH_3)_3C{-}C{\equiv}C]_2C{=}CH\underset{\underset{\displaystyle O}{\|}}{C}C(CH_3)_3.$$

The conversion of the carbinol into tri-*tert.*-butylethynylbromomethane was attempted by the use of phosphorus tribromide according to the procedure described by Gray and Marvel[3] for the corresponding chloride, and also by the use of acetyl bromide. Both procedures gave two isomeric bromides which were separated by differences in their solubility.

Qualitative tests with alcoholic silver nitrate indicated that the low melting bromide was the more reactive, and this suggested that it was the desired tri-*tert.*-butylethynylmethyl bromide. Attempts to convert either compound into the original carbinol by means of silver oxide were unsuccessful, probably due to their sensitivity toward oxidation by this reagent. It was possible, however, to convert the low melting bromide into an acetate by the action of silver acetate in boiling benzene. Tri-*tert.*-butylethynylmethyl acetate (II) was then prepared by the action of acetyl chloride or acetic anhydride on the sodium or potassium derivative of tri-*tert.*-butylethynylcarbinol (I), and its structure was proved by hydrolysis to the original carbinol by means of potassium ethylate,



according to the method described by Moureu, Dufraisse and Houghton.[6] This ester was found to be identical with that prepared from the low melting bromide, thus establishing the structure of this latter compound as tri-*tert.*-butylethynylbromomethane (III).

The bromide (III) was found to react with molecular silver to give hexa-*tert.*-butylethynylethane (IV). Solutions of the ethane showed no tendency to absorb oxygen at room temperature. The tests of dissociation at higher temperatures were found to be of no value because of a tendency of the compound to rearrange on heating to give an isomeric hydrocarbon.

Recently, Conant and Garvey[7] have developed a semi-quantitative method for determining the strength of the carbon–carbon linkage in substituted ethanes which is based on the differential cleavage by alloys of alkali metals to give metallic alkyls. The reaction of these alloys on hexa-*tert.*-butylethynylethane was tested in ether solution in accordance with their directions. As shown in Table I, cleavage of the ethane linkage to give the highly colored metallic alkyl (VI) was found to take place in every case.

TABLE I

ACTION OF ALLOYS OF ALKALI METALS ON AN ETHER SOLUTION OF HEXA-*tert.*-BUTYLETHYNYLETHANE

Alloy	First coloration	Appearance of red color	Total time shaken	Yield of crude acid
K·Na	Instantaneous	2 minutes	16 hours	70–90%
40% Na(Hg)X	3 minutes	4 hours	9 hours	Not accurately determined
1% Na(Hg)X	4 hours	Several days	9 days	About 10%

The metallic alkyl when treated with dry carbon dioxide and decomposed with water and hydrochloric acid yielded tri-*tert.*-butylethynylacetic acid (V). The structure of this acid was established by proving its identity with a sample of the acid prepared from tri-*tert.*-butylethynylbromomethane by the action of magnesium and carbon dioxide. From a comparison of these results with those reported by Conant and Garvey,[7] it can be concluded that the stability of the ethane carbon linkage in hexa-*tert.*-butylethynylethane is intermediate between that of dibenzyl and hexaphenylethane.

As yet the exact structures of the higher melting isomers of the bromide and of the ethane obtained by heating the solutions of the corresponding lower melting isomers (Formulas III and IV) have not been determined. This phase of the problem is now under investigation.

Experimental Part

Tri-*tert.*-butylethynylcarbinol.—Forty g. of *tert.*-butylacetylene was added from a dropping funnel to 135 cc. of a 3.673 *N* ether solution of ethylmagnesium bromide during

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[6] Moureu, Dufraisse and Houghton, *Bull. soc. chim.*, [4] 41, 55 (1927).

[7] Conant and Garvey, THIS JOURNAL, 49, 2080, 2599 (1927).

two hours. The heat of the reaction was sufficientto cause the ether and acetylene to **reflux** and this necessitated the use *of* a very efficient condenser cooled with water at 5°. The **mixture** usually solidified, presumably due to the precipitation of the *tert.*-butylethynylmagnesium bromide. **Half** of the theoretical amount of ethyl chlorocarbonate was then carefully added and the mixture was stirred overnight. Then the remainder of the ethyl chlorocarbonate was added during three or four hours. The mixture was decomposed by pouring it into cracked ice and adding the theoretical amount of dilute hydrochloric acid. The ether layer was dried over sodium sulfate and heated on a steam-bath to remove the solvent. The residue was distilled under reduced pressure and the fraction which boiled at 131–140° at **12** mm., or 122–124° at **4** mm., was collected and recrystallized from hexane or petroleum ether. The yield was 18–23 g. (40–50% of the theoretical amount); m. p. 100–102.2° (corr.). The vacuum distillation was omitted in several of the runs and purification carried out entirely by crystallization. Practically the same yield and purity of product were obtained.

Double Salt from the **Carbinol** and **Stannic** Chloride.—An excess of freshly distilled stannic chloride was added to **0.5** g. of **tri-*tert.*-butylethynylcarbinol** in benzene. A brown precipitate appeared. This was collected on a suction filter and washed with anhydrous ether. The color was thus removed and a white crystalline product remained.

Anal. Subs., **0.1407, 0.1185: 10.71, 9.1 cc.** of **0.0993** *N* **$AgNO_3$.** Calcd. for **$C_{19}H_{28}O{\cdot}SnCl_4$: Cl, 26.66.** Found: **Cl, 26.79, 27.02.**

Rearrangement of the **Carbinol** with Sulfuric Acid.—Two g. of tri-*tert.*-butylethynylcarbinol was dissolved in **10** cc. of glacial acetic acid and **1** cc. of **concd.** sulfuric acid was added with cooling. A precipitate formed and the mixture was poured onto **20** g. of cracked ice. The organic material was collected in petroleum ether and this solution was evaporated to **15 cc.** and cooled. The yellow product which separated was recrystallized three times from petroleum ether. It then melted at 109.5–110.5 (corr.) and gave no reaction when treated with metallicsodium in the cold.

Anal. Subs., **0.1366: CO_2, 0.4167; H_2O, 0.1248.** Calcd. for **$C_{19}H_{28}O$: C, 83.75; H, 10.36.** Found: C, 83.20; H, 10.22.

Tri-*tert.*-butylethynylbromomethane.—Three g. of the carbinol was **dissolved** in **25** ec. of petroleum ether and stirred for one-half hour with **1** g. of phosphorus tribromide at **0°.** To the mixture was added **100** cc. of 10% sodium bicarbonate solution and stirring was continued for ten minutes. The petroleum ether layer was then separated, dried over sodium sulfate and evaporated to dryness under reduced pressure at room temperature. The residue was dissolved in the minimum quantity of absolute ether and **5** cc. of absolute alcohol was added. This solution was evaporated under diminished pressure until crystals began to form and then cooled at **0°** overnight, The bromide **was** collected on a filter and dried in a vacuum desiccator, The yield was 2 g. **(54%** of the **theoretical** amount); m. p. 66.5–68.5 (corr.). This product was **sufficiently** pure for most purposes, but the sample used for analysis was recrystallized several times from alcohol and ether and then melted at 69–70° (corr.).

Anal. Subs., **0.1597: CO_2, 0.3967; H_2O, 0.1158.** Calcd. for **$C_{19}H_{27}Br$:** C, **68.04;** H, 8.12. Found: **C, 67.74; H, 8.11.**

Anal. (**Parr** bomb). Subs., **0.3475: 10.27** cc. of **0,0993** N $AgNO_3$. Calcd. for **$C_{19}H_{27}Br$:** Br, **23.85.** Found: Br, **23.45.**

Mol. wt. **(Rast method).**[8] Subs., 0.0112, camphor, **0.1040:** A T (depression), **13.3** (average of two observations); constant for camphor, **40.** Calcd. for **$C_{19}H_{27}Br$:** mol. **wt., 335.** Found: **324.**

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[8] Rast, *Ber.*, **55,1051,3727 (1922).**

High Melting Bromide from Carbinol.—The alcoholic mother liquor from the crystallization of tri-*tert*.-butylethynylbromomethane was allowed to evaporate at room temperature and the red, viscous mass which remained was dissolved in hot acetone, filtered and allowed to cool. The product which crystallized out was further purified by recrystallizations from acetone; m. p. 177–178° (corr.).

Anal. (Parr bomb). Subs., 0.2992, 0.3743: 8.67, 10.79 cc. of 0.1045 N $AgNO_3$. Calcd. for $C_{19}H_{27}Br$: Br, 23.85. Found: 24.17, 24.07.

This same compound was obtained by dissolving the lower melting bromide in absolute alcohol and heating for about an hour at 100° in a sealed tube.

Tri-*tert*.-butylethynylmethyl Acetate. (A) From **Tri-*tert*.-butylethynylcarbinol.**—Two g. of the carbinol was added to a suspension of 1 g. of powdered potassium in petroleum ether (b. p. 60–70°) and stirred for five to ten minutes. The supernatant liquid was decanted and treated with 2 cc. of acetic anhydride with stirring. The mixture was decomposed with water, neutralized with sodium bicarbonate solution and the upper layer dried with sodium sulfate, evaporated to 5 cc. and cooled. The ester crystallized. The yield was 1.2 g., m. p. 143–144° (corr.). Two recrystallizations from acetone raised the m. p. to 144.5–145.5° (corr.).

Anal. Subs., 0.1760: CO_2, 0.5186; H_2O, 0.1674. Calcd. for $C_{21}H_{30}O_2$: C, 80.21; H, 9.96. Found: C, 80.35; H, 10.01.

(B) From **Tri-*tert*.-butylethynylbromomethane.**—One g. of dry, pulverized silver acetate and 0.8 g. of the bromide, m. p. 70–71° (corr.). were refluxed in benzene for twenty-four hours. The solvent was evaporated under reduced pressure and the residue crystallized from petroleum ether, giving 0.1 g. of product melting at 142–143° (corr.). A mixture of this product with the ester obtained from the carbinol melted at 143.5–144.5° (corr.).

Hydrolysis of Tri-*tert*.-butylethynylmethyl Acetate.—Attempts to hydrolyze the ester with alcoholic solutions of potassium hydroxide or barium hydroxide were unsuccessful. The method of hydrolysis described by Moureu[6] was followed. One g. of the ester was shaken mechanically for twelve hours with 10 cc. of a saturated solution of potassium ethylate in alcohol. The resulting solution was decomposed with dilute sulfuric acid and the carbinol crystallized from petroleum ether. It melted at 101° and showed no depression of the melting point when mixed with known tri-*tert*.-butylethynylcarbinol.

Hexa-*tert*.-butylethynylethane.—Two g. of tri-*tert*.-butylethynylbromomethane was shaken mechanically with 2 g. of molecular silver[9] in 10 cc. of absolute ether for twenty-four hours. The ether was evaporated under reduced pressure almost to dryness and 5 cc. of absolute alcohol was added. The evaporation was continued until crystallization began and then the mixture was cooled. The yield was 0.7 g. (46% of the theoretical amount); m. p. 130–131° (corr.).

Benzene was also used as the reaction solvent but this solvent had to be completely removed or difficulty was found in the subsequent crystallization. The condensation was carried out both in the presence of nitrogen and in the presence of air, but no difference in the yield or nature of the product could be detected. Zinc dust was found to have no action on the bromide.

Anal. Subs., 0.1596: CO_2, 0.5214; H_2O, 0.1554. Calcd. for $C_{38}H_{54}$: C, 89.34; H, 10.66. Found: C, 89.09; H, 10.94.

Mol. wt. (Cryoscopic in benzene). Subs., 0.0981, 0.2401; benzene, 12.9452: ΔT (depression), 0.079, 0.181°. Constant for benzene: 5.12. Calcd. for $C_{38}H_{54}$: Mol. wt., 510. Found: 491, 525.

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[9] Vanino, "Preparativen Chemie," F. Enke, Stuttgart, 1913, Vol. I, p. 417.

Mol. wt. (Rast method). Subs., **0.0114;** camphor, **0.1174.** A T (depression). **8.0°;** constant for camphor, **40.** Pound: Mol. wt., **485.**

In the first run of this condensation, the reaction mixture, after twenty-two hours' shaking, was tested for oxygen absorption. The oxygen was introduced from a gas buret and the mixture agitated for two hours. There was no decrease in the volume of oxygen and the unchanged ethane was isolated in a **32%** yield.

The Rearranged Hydrocarbon.—A solution of **0.1** g. of the ethane in 1 cc. of xylene **was** heated in an atmosphere of nitrogen in order to test for the appearance of color indicating thermal dissociation. The solution turned slightly yellow at **120°**, and bright yellow at 140°. The color was not discharged on cooling. Evaporation of the solvent left a residue which after crystallization from alcohol melted at 172–174° (corr.). The same compound was obtained by heating the ethane in alcohol. One-tenth g. of the ethane and **3–5** cc. of absolute alcohol were heated for one hour in a sealed tube immersed in boiling water. The contents were poured into a small beaker and cooled below 0°. The yield of rearranged hydrocarbon was **40–60%** of the theoretical amount, m. p. **172–174"** (corr.). Recrystallization raised the m. p. to 174–175° (corr.).

Anal. Subs., **0.1221:** CO_2, **0.3975;** H_2O, **0.1169.** Calcd. for $C_{38}H_{64}$: C, **89.34;** H, **10.66.** Found: *C*, **88.78;** H, **10.71.**

Mol. wt. (Cryoscopic in benzene). Subs., **0.0822;** benzene, **12.8369;** A T (depression), **0.065";** constant for benzene, **5.12.** Calcd. for $C_{38}H_{64}$; mol. wt., **510.** Found: 504.

Cleavage of Hexa-*tert.*-butylethynylethane with Metals.—The tests for cleavage were carried out in a **50-cc.,** round-bottomed flask. Absolute ether distilled over ethylmagnesium bromide was used as a solvent, and the air was replaced by dry, oxygen-free nitrogen. The proportions used were those suggested by Conant and Garvey,[7] **0.1** g. ethane, **1** cc. of liquid alloy and **10** cc. of solvent. The flask containing this reaction mixture was shaken mechanically at the rate of **320** oscillations per minute. The results with different alloys have been recorded in Table I.

Tri-*tert.*-butylethynylacetic Acid (A) from Hexa-*tert.*-butylethynylethane.—Five **cc.** of potassium–sodium (10/4) alloy and **0.57** g. of the ethane were shaken in ether for sixteen hours. Dry carbon dioxide was passed into the mixture for three hours, and the mixture decomposed carefully with moist carbon dioxide, moist ether and finally dilute hydrochloric acid. The ether layer was evaporated with a solution of **1** *g.* of potassium hydroxide in **10** cc. of water. The alkaline solution was filtered and the filtrate was acidified with hydrochloric acid. The acid thus precipitated was yellow to red in color and weighed **0.39** g. **(70%** yield). It was reprecipitated twice from alkaline solution with hydrochloric acid and recrystallized once from dilute methyl alcohol using some decolorizing carbon (Norit). The product thus obtained was still yellow in color but treatment with Norit in petroleum ether completely removed the color and gave a product melting at 202–205° (corr.).

(B) From Tri-*tert.*-butylethynylbromomethane.—In a **25** cc., three-necked, roundbottomed flask, were placed **1.52** g. of the bromide, **0.26** g. of magnesium, **0.09 g.** of iodine and **10** cc. of dry ether. Stirring was begun and a slow stream of *dry* carbon dioxide was passed over the solution for seven hours. The mixture was decomposed with dilute hydrochloric acid and the organic acid was reprecipitated twice from the aqueous solution of its potassium salt. The product was recrystallized once from methyl alcohol and three times from petroleum ether (using Norit), after which it melted at 201–203° (corr.). A mixture of the acid from (A) and (B) melted at 201–204° (corr.).

Neutral Equivalent. Subs., **0.2463:** **7.21** cc. of **0.1138** N NaOH. Calcd. for $C_{20}H_{28}O_2$: **300.2.** Pound: **300.5.**

The acid was recovered and recrystallized from petroleum ether, m. p., 202–205° (corr.).

Anal. Subs., 0.0931: CO_2, 0.2708; H_2O, 0.0805, Calcd. for $C_{20}H_{28}O_2$: C, 79.94; H, 9.40. Found: C, 79.32; H, 9.67.

Summary

1. Hexa-*tert.*-butylethynylethane has been prepared and has been shown to be undissociated at room temperature and to undergo rearrangement at elevated temperatures.

2. Cleavage by alkali metals has indicated that the stability of the central ethane linkage is intermediate between that of the corresponding linkages in dibenzyl and hexaphenylethane.

URBANA, ILLINOIS

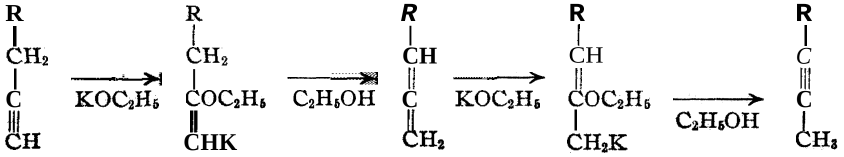
[CONTRIBUTION FROM THE LABORATORY OR THE J. B. WILLIAMS COMPANY]

REARRANGEMENTS OF THE TRIPLE BOND

BY HERBERT H. GUEST

RECEIVED MARCH 5, 1928 PUBLISHED JUNE 5, 1928

There are two types of the higher homologs of acetylene, the so-called true or monosubstituted acetylenes, $RC{\equiv}CH$ (I), and the iso-acetylenes $RC{\equiv}CR''$ (II). That the one type may be transformed into the other was first observed by Favorsky,[1] who effected the rearrangement of type I into type II by the action of alcoholic potash and the reverse rearrangement with metallic sodium. His explanation of the former rearrangement postulated the presence of alcohol in the reaction mixture as essential. He stated that solid alkalies were unable to effect it. His scheme is represented as follows



He also found that there was a minimum temperature, characteristic for each acetylene, below which, if rearrangement proceeds at all, it must be extremely slow.

Wislicenus and Schmidt,[2] were unable to confirm Favorsky's statement that ethylacetylene is completely rearranged by alcoholic potash. These workers found some unaltered material in their reaction product.

Bourguel[3] states that sodamide acting on dihalides leads only to the formation of monosubstituted acetylenes, type I. This result is not in accord with the experience of the writer.[4] Some of type II was in-

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[1] Favorsky, *J. prakt. Chem.*, [2] 37, 382, 417 (1888).

[2] Wislicenus and Schmidt, Ann., 313, 220 (1900).

[3] Bourguel, Ann. *Chemie* [10] 3, 191, 325 (1925).

[4] Guest, THIS JOURNAL, 47, 862 (1925).

variably produced by this method. Apparently no worker in this field has questioned the finality of Favorsky's work upon these rearrangements until the work of Hill and Tyson[5] on the vapor phase dehalogenation of dichloroheptane appeared. These authors found that instead of the expected type I heptine they obtained as the major product isoheptine, confirming some previous unpublished results of the present writer. They raised the question whether the heptine, undoubtedly the primary product of the dehalogenation, does not undergo a thermal rearrangement.

To determine whether the rearrangement from type I to type II could be brought about in the complete absence of alcohol, the writer conducted experiments under conditions identical with those described by Hill and Tyson.[5] Thus, by passing a hydrocarbon mixture of predetermined heptine content over soda lime, and observing the increase of *iso*heptine, it was found that rearrangement proceeded to the extent of 70%. Further, when pumice replaced soda lime, some rearrangement took place but not as smoothly or to as great extent as in the previous case. The probable reason for Favorsky's negative result with dry alkalies is that his reaction temperatures were too low.

The rearrangement from iso-form II to true form I is brought about, according to Favorsky,[1] by the action of sodium at temperatures slightly above 100° and also by sodamide at 160°.[3] This reagent Bourguel found causes a rearrangement of the triple bond to the end of the chain, for example, $RC{\equiv}CC_2H_5 \longrightarrow R(CH)_2C{\equiv}CH$, but not quantitatively. The length of time and temperature required vary with each acetylene. The iso-form obtained by the writer by vapor phase rearrangement was changed back to true heptine by sodamide to the extent of 65% of theoretical.

The proportion of each form was determined by the method of Behal,[6] recently improved by Hill and Tyson,[5] which depends upon the insolubility of the silver derivative of the type I acetylene in alcohol with liberation of the equivalent amount of nitric acid.

The evidence presented seems to indicate that the rearrangement from one form to another, in the absence of alcohol, is to be explained on the same basis as the corresponding olefinic rearrangement, $RCH{=}CH_2 \rightleftarrows R'CH{=}CHR''$, with the exception that in the case of the acetylene of type I an inert sodium derivative can be formed, which fact facilitates the rearrangement of type II to type I.

Incidentally, a general method for the synthesis of the higher homologs of acetylene was developed, which may be represented as follows

$$RMgBr + CH_2{=}CHCH_2Br \longrightarrow RCH_2CH{=}CH_2 \xrightarrow{Br}$$

$$RCH_2CHBrCH_2Br \xrightarrow{KOH} RCH_2C{\equiv}CH$$

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[5] Hill and Tyson, This Journal, 50, 172 (1928).

[6] Behal, *Ann. chim. phys.*, [6] 15, 424 (1888).

The novel feature of this method is the use of finely powdered potassium hydroxide suspended in mineral oil as dehalogenation reagent.

Experimental Part

Preparation of **Heptine.**—A three-necked flask was fitted with a mechanical stirrer, a dropping funnel and a distillation column leading to a condenser. In it were placed 100 g. of finely powdered potash and 200 cc. of mineral oil. The temperature was raised to 250° (oil-bath) and 50 g. of dibromoheptane added slowly, the agitation being continued until no more oil distilled over; weight of distillate, 15 g., which is 81% of the theoretical. This distillate was found on analysis to contain 74% of heptine. This method has been found to give equally good results in the preparation of other acetylenes, for example, pentine.

Rearrangement of Heptine, $CH_3(CH_2)_4C\equiv CH$, to Isoheptines over Soda Lime.—Fourteen g. of a mixture of isoheptine and heptine, containing 90% of the latter, was slowly dropped into an iron tube filled with 280 g. of soda lime (50% NaOH). The tube was heated to 380°. (This tube was loaned by Professor A. J. Hill of Yale University and has been fully described by him.[5] The writer desires to express his thanks to Professor Hill.) The distillate was returned to the tube for a second treatment before final fractionation. There was obtained 11 g. of material, boiling over 100–110°. This fraction was analyzed by the method previously described and 16.5% of heptine was found. At a temperature of 250" there was practically no rearrangement.

Thermal Rearrangement of Heptine without a **Catalyst.**—On passing heptine (90% pure) through the tube, filled with large pieces of pumice and heated to 350°, there was a copious evolution of white fumes. The product was washed with water and distilled. It commenced to come over at a lower temperature. The heptine–isoheptine fraction was subjected to a carbon and hydrogen determination to verify its essential purity. This fraction showed a heptine content of 68%.

Rearrangement of Isoheptines to Reptine.—The mixture obtained from the rearrangement over soda lime, which contained upwards of 80% of isoheptine, was heated for twelve hours at 160° with finely divided sodamide suspended in 35 cc. of mineral oil, with mechanical agitation. After washing and distillation, the oil was analyzed. Heptine was present to the extent of 64%.

Summary

1. It has been found that true acetylenes $RC\equiv CH$ are changed into *iso*-acetylenes $R'C\equiv CR''$, in the absence of alcohol, by vapor phase thermal rearrangement. Further work upon the mechanism of rearrangement is in progress.
2. A general method for the preparation of acetylenes is given.

GLASTONBURY, CONNECTICUT

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

THE KETAZINES OF LEVULINIC ACID AND OF LEVULINIC HYDRAZIDE

BY CHESTER WALLACE BENNETT

RECEIVED MARCH 8, 1928 PUBLISHED JUNE 5, 1928

Having occasion to prepare the hydrazone of fluorenonecarboxylic acid-2, it was thought best to gain experience by preparing the hydrazone of a less expensive keto acid. Levulinic acid was selected. So far as could be determined, no keto acid hydrazone has ever been obtained. Curtius —attempted the preparation of the hydrazone of pyruvic acid, $CH_3COCOOH$. He treated barium pyruvate with hydrazine sulfate and did not obtain the hydrazone, but instead a compound of unknown structure, of empirical composition, $C_5H_{10}N_2O_3$. When he treated the free acid with hydrazine hydrate, he obtained the hydrazine salt of the hydrazone. He was unable to prepare the acid hydrazone from this. The reason seems apparent from the results reported in this article.

Later,[2] in working with ethyl levulinate, he found that hydrazine hydrate converts it into the hydrazide of levulinic acid, $CH_3COCH_2CH_2CONHNH_2$, m. p. 82°, just as ammonia converts an ester into an amide. The ketonic group is apparently untouched.

It is also generally known that any organic acid if boiled with hydrazine hydrate forms the hydrazide.

$$RCOOH + N_2H_5OH = RCONHNH_2 + 2H_2O$$

It would be necessary, therefore, in preparing the hydrazone of levulinic acid to cover the carboxyl group to prevent the formation of the hydrazide. The sodium salt of the acid was treated with hydrazine hydrate and then carefully acidified to obtain the free acid. In ten reactions under various conditions no hydrazone was found, but in all cases various amounts were formed of the ketazine of levulinic acid, $HOOCCH_2CH_2C(CH_3){=}N{-}N{=}C(CH_3)CH_2CH_2COOH$.

The ketazine is a new compound. It is very easily hydrolyzed in hot, water and slowly even by the moisture of the air, since it is very hygroscopic. The hydrolytic products are the hydrazide and free levulinic acid.

Experiments starting with the free acid and also with the hydrazide resulted in the formation of the ketazine of the hydrazide in both cases and none of the salt nor of the hydrazone was obtained.

Attempts to Prepare the Hydrazone of Levulinic Acid.—To a solution of 2 g. of sodium in 25 cc. of 95% alcohol, 10 g. of levulinic acid was added. After five minutes, 15 cc. of 40% hydrazine hydrate was added and the mixture refluxed for sixteen hours

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[1] Curtius, *J. prakt. Chem.*, [2] 44, 555 (1891).

[2] Curtius, *ibid.*, [2] 50, 522 (1894).

on a water-bath. The alcohol, water and excess hydrazine hydrate were now distilled at reduced pressure and the dry salt dissolved in a very small amount (10 cc.) of ice water. Then slowly, cooling with an ice and salt mixture, 22 cc. of 6 N hydrochloric acid was added from a buret. A white precipitate began to form and quickly increased in amount until 6.5 g. was obtained, of melting point 112–114°. This represents a 58% yield of the ketazine of levulinic acid.

A second run, in which the precipitate was washed more carefully, yielded 4 g. melting at 119–120° (corr.). It was insoluble in ether or petroleum ether and practically insoluble in cold alcohol or water. On boiling with either of the latter, however, it is quantitatively changed to the hydrazide of levulinic acid, m. p., 81–82', and levulinic acid. It is also very hygroscopic and is almost completely hydrolyzed in a few days by the moisture thus absorbed.

Anal. Calcd. for $C_{10}H_{16}O_4N_2$: N, 12.28. Found: 12.36.

Mol. wt. By titration: calcd.: 228. Found: 230.

Attempts to Prepare the Hydrazone of the Hydrazide of Levulinic Acid.—In a 200 cc. round-bottomed flask fitted with a reflux condenser. 10 cc. of 50% hydrazine hydrate was placed and then slowly from a dropping funnel, 6.5 g. of the hydrazide of levulinic acid in 16 cc. of alcohol was added. The mixture was then refluxed for twenty hours. The solution was filtered and allowed to cool, whereupon colorless crystals melting at 217–219° (corr.) were obtained. Later the following simpler method was used.

A solution of 11.6 g. of levulinic acid in 5 cc. of alcohol was added to 35 cc. of 50% hydrazine hydrate on a water-bath. After twenty hours' refluxing and proceeding as above, a white crystalline solid amounting to 1 g. was obtained. After boiling up twice with absolute alcohol to remove impurities, a product insoluble in alcohol, water, ether, etc., melting at 219–220° (corr.) resulted. It is identical with that formed from the hydrazide, as is shown by a mixed melting point test. The product is neutral and does not blacken yellow mercuric oxide, reduce Fehling's solution, nor form a condensation product with benzaldehyde, thus showing that it is neither a hydrazine salt nor a hydrazone. The analysis showed it to be the ketazine of the hydrazide of levulinic acid, the formula of which is $NH_2NHCOCH_2CH_2C(CH_3){=}N{-}N{=}C(CH_3)CH_2CH_2CONHNH_2$.

Anal. Calcd. for $C_{10}H_{20}O_2N_6$: N, 32.81. Found: 32.30.

Mol. wt. By freezing point depression of glacial acetic acid, calcd.: 256. Found: 254.8.

This work was undertaken at the suggestion of Professor W. A. Noyes.

Summary

1. Attempts to prepare the hydrazone of levulinic acid resulted in the formation of the ketazine of the acid.

2. Attempts to prepare the hydrazone of the hydrazide of levulinic acid and also of the hydrazine salt of the acid resulted in the formation of the ketazine of levulinic hydrazide.

3. The following new compounds were prepared: (a) the ketazine of levulinic acid, $C_{10}H_{16}O_4N_2$, m. p. 119–120° (corr.); (b) the ketazine of levulinic hydrazide, $C_{10}H_{20}O_2N_6$, m. p. 219–220° (corr.).

URBANA, ILLINOIS

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

THE STRUCTURES OF CONVOLVULINOLIC AND JALAPINOLIC ACIDS. SYNTHESIS OF 11-HYDROXYPENTADECANOIC AND 11-HYDROXYHEXADECANOIC ACIDS

BY LETHA A. DAVIES[1] AND ROGER ADAMS

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The roots of various plants of the *Convolvulaceae* family contain glucosidic resins which have been used medicinally as purgatives for many centuries. The plants are cultivated in Mexico, Jamaica and South America, and also grow wild on the eastern slopes of the Mexican Andes.

Perhaps the most important of the resins are jalap resin, occurring in *Tubera Jalapae,* and the resins obtained from Orizaba root, Scammonium and Tampicojalap. Since the beginning of the nineteenth century these resins have been the subject of many chemical investigations, the earliest of which were concerned chiefly with the extraction of the resins from the tubers.[2] The products of hydrolytic decomposition were studied in Liebig's Laboratory as early as 1844.[3]

The resin from Orizaba root yields on hydrolysis an hydroxyhexadecanoic acid, jalapinolic acid, investigated by Kromer.[4] On reduction of this acid Kromer obtained a hexadecanoic acid which he reported as not identical with palmitic acid. On oxidation the jalapinolic acid gave substances which he believed to be identical with methylethylacetic and sebacic acids. Accordingly Kromer suggested for jalapinolic acid the formula $CH_3CH_2CH(CH_3)CHOH(CH_2)_{10}CO_2H$.

Taverne[5] and Hoehnel[6] worked on the jalap resin, which is now called convolvulin. The chief product of hydrolytic decomposition of convolvulin is an hydroxypentadecanoic acid, convolvulinolic acid. These investigators studied its oxidation and obtained what they assumed to be methylethylacetic acid and an isomer of sebacic acid. As a result of these researches, the structure of convolvulinolic acid was suggested as $CH_3CH_2CH(CH_3)CHOH(CH_2)_9CO_2H$.

Power and Rogerson[7] examined jalap resin and in their investigations reported the isolation of convolvulinolic acid and the preparation of its

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[1] This communication is an abstract of a portion of a thesis presented by Letha A. Davies in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Cadet de Gassicourt, J. *pharm.*, [2] 3, 495 (1817); Nativelle, J. *pharm. chim.*, [3] 1, 228 (1842).

[3] Kayser, *Ann. Chem. Pharm.*, *51*, 81 (1844). See also Mayer, *ibid.*, 83, 121 (1852); 92, 125 (1854); 95, 129 (1855).

[4] Kromer, J. *prakt. chem.*, [2] *57*, *448* (1898).

[5] Taverne, *Rec. trav. chim.*, 13, 187 (1894).

[6] Hoehnel, *Arch. Pharm.*, 234, 647 (1896).

[7] Power and Rogerson, THIS JOURNAL, **32**, 80 (1910).

methyl ester. They assumed the structure assigned by Hoehnel to be correct. A little later the same authors[8] studied scammony root and isolated jalapinolic acid. In this paper the results of a study of the optical rotation of jalapinolic and convolvulinolic acids were reported. Both acids were found to be optically active, a fact which had been overlooked by previous investigators, due possibly to very low values obtained. In a third paper[9] the preparation of methyl jalapinolate and the determination of its optical activity were described.

Y. Asahina[10] and collaborators have recently published the results of their investigations into the structures of convolvulinolic and jalapinolic acids. These acids were reduced with hydriodic acid and red phosphorus and the products obtained were reported by these authors to be n-pentadecanoic and n-hexadecanoic acids, respectively, identified by melting points of the acids themselves and of their anilides. The hydroxy acids were oxidized to the corresponding keto acids, then converted to the oximes and allowed to undergo the Beckmann rearrangement. The resulting acid amides were decomposed and yielded in the case of convolvulinolic acid, nonanedicarboxylic and 10-aminodecanoic acids and, in the case of jalapinolic acid, nonanedicarboxylic and 10-aminodecanoic acids, along with a small amount of caproic acid. On the basis of these experiments the formulas suggested by these authors were 11-hydroxyhexadecanoic acid (I) for jalapinolic acid and 11-hydroxypentadecanoic acid (II) for convolvulinolic acid.

$$\underset{\text{I}}{CH_3(CH_2)_4CHOH(CH_2)_9CO_2H} \qquad \underset{\text{II}}{CH_3(CH_2)_3CHOH(CH_2)_9CO_2H}$$

The present work was undertaken with the object of synthesizing the two acids having the formulas I and II. These acids have been made by the general procedure developed recently in this Laboratory for synthesizing hydroxy acids.[11] Methyl 10-aldehydodecanoate[11c] was condensed with (a) n-amyl magnesium bromide and (b) n-butyl magnesium bromide, and the methyl esters of the hydroxy acids thus produced were then saponified.

$$\text{(a)}\quad CH_3(CH_2)_4MgBr + CHO(CH_2)_9CO_2CH_3 \longrightarrow CH_3(CH_2)_4CHOH(CH_2)_9CO_2CH_3$$
$$\text{(b)}\quad CH_3(CH_2)_3MgBr + CHO(CH_2)_9CO_2CH_3 \longrightarrow CH_3(CH_2)_3CHOH(CH_2)_9CO_2CH_3$$

The acids and esters thus obtained were, of course, racemic and consequently might be expected to have different constants from the corresponding natural acids and esters which are optically active. The identity or non-identity of the general structures of the synthetic molecules

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[8] Power and Rogerson, J. *Chem. Soc.*, 101, 1 (1912).

[9] Power and Rogerson, J. *Chem. Soc.*, 101, 398 (1912).

[10] Asahina, J. Pharm. *Soc.* Japan, 523, 779 (1925); *C.* A., 20, 365, 366 (1926).

[11] (a) Noller with Adams, THIS JOURNAL, 48, 1074 (1926); (b) Hiers with Adams, *ibid.*, 48, 1089, 2385 (1926); (c) Tomecko with Adams, *ibid.*, 49, 522 (1927).

with the natural was, however, readily established. Upon oxidation of the convolvulinolic and jalapinolic acids the corresponding keto acids were produced which, if the structures assigned the natural acids by Asahina are correct, should be optically inactive. The keto acids produced, moreover, should be identical with the keto acids formed by oxidation of synthetic I1-hydroxypentadecanoic acid and I1-hydroxyhexadecanoic acid. Reduction of the keto acids made from the natural acids should yield hydroxy acids identical with the synthetic compounds. The constants of these various compounds are given in Table I.

TABLE I

MELTING POINTS OR NATURAL AND SYNTHETIC COMPOUNDS

	Jalapinolic acid, °C.	11-Hydroxyhexadecanoic acid, °C.	Convolvulinolic acid, °C.	11-Hydroxypentadecanoic acid, °C.
Acid	65.5–66 5	68–69	51–52	63.5–64
Methyl ester	46–47	40.5–41.5	31–32	about 2932
Ketone by oxidation	74–75	74–75	63–64	70–71
Hydroxy from reduction of ketone	68–69	....	51–52[a]	....

[a] Although the melting point of this substance is the same as that of the original convolvulinolic acid, a mixed melting point proved the two hydroxy acids to be different. The melting point was obtained after three recrystallizations from ethyl acetate. The small quantity of material, however, did not permit further investigation.

It is seen that the keto acids from jalapinolic acid and 11-hydroxyhexadecanoic acid have the same melting point, and a mixed melting point shows them to be identical. Moreover, reduction of the keto acid from jalapinolic acid gives an hydroxy acid identical in melting point with 11-hydroxyhexadecanoic acid, and a mixed melting point shows no depression. It is thus definitely established that jalapinolic acid is the d-form of 11-hydroxyhexadecanoic acid.

On the other hand, the keto acids from convolvulinolic acid and from 11-hydroxypentadecanoic acid do not melt at the same point and a mixed melting point gives a marked depression. The reduced keto acid from convolvulinolic acid melts at a different point from 11-hydroxypentadecanoic acid and the mixed melting point is lower than either. It appears, therefore, that convolvulinolic acid is not 11-hydroxypentadecanoic acid. A further study of this substance is now being made.

Worthy of mention is a slight modification of the procedure used in the condensation of aldehyde esters with the Grignard reagent in order to improve the yields of pure product. Where no particular precautions were observed in the condensation of the butylmagnesium or amylmagnesium bromide with methyl 10-aldehydodecanoate, in spite of the fact that the alkyl bromides were pure and the methyl 10-aldehydodecanoate boiled within two degrees, low yields of esters distilling over a wide range were obtained. Upon saponifying, acids were obtained in very low yields. They proved to be the keto acids instead of the expected hydroxy acids. Such formation is extraordinary and unexpected and can only be explained by the presence of acid ester in the aldehyde ester.

$$HO_2C(CH_2)_9CO_2CH_3 + 2RMgBr \longrightarrow BrMgOCO(CH_2)_9CO_2CH_3 \longrightarrow RCO(CH_2)_9CO_2CH_3$$

This would also account for the low yields of product. The lower solubility of the keto acid as compared with the hydroxy acid renders its isolation easy.

If the aldehyde ester was carefully extracted with 10% sodium carbonate, then worked up and distilled twice in an atmosphere of nitrogen and immediately condensed and carried through to the final product in an atmosphere of nitrogen, the hydroxy esters were obtained readily and in a pure state.

In the course of these investigations, when the exact character of the products obtained from the condensations of the aldehyde ester with Grignard reagents was doubtful, it seemed desirable to prepare the keto acids by some other method. Accordingly, the reaction between an acid chloride and a Grignard reagent was used, and 9-ketohexadecanoic acid was prepared in a trial run by this method. Directions for this condensation were furnished by John R. Johnson.[12]

The authors are deeply indebted to Professor Asahina for his kindness in sending them samples for melting-point determinations, of the compounds used in his investigations, and to Dr. C. G. Tomecko for furnishing generous samples of jalapinolic and convolvulinolic acids.

Experimental Part

Methyl 10-Aldehydodecanoate.—This was prepared in 60% yields by the ozonation of methyl 11,12-dodecenoate according to the general procedure described by Noller and Adams[11a] for preparing aldehyde esters. The methyl 11,12-dodecenoate was synthesized from ethyl undecenoate by the method of Tomecko and Adams.[11c] The aldehyde ester used in these experiments was carefully freed from acid ester by extraction of the ethereal solution with 10% sodium carbonate. The subsequent distillations were carried out in an atmosphere of nitrogen; the product, on second distillation, boiled at 141–143° at 4 mm.

Methyl 11-Hydroxyhexadecanoate, $CH_3(CH_2)_4CHOH(CH_2)_9CO_2CH_3$.—A solution of 50 g. of pure methyl 10-aldehydodecanoate in 500 cc. of anhydrous ether was treated with an equivalent amount (determined by titration of the Grignard solution[13]) of n-amyl magnesium bromide, according to the directions of Noller and Adams,[11a] except that the condensation was carried out in an atmosphere of nitrogen. The hydroxy ester obtained was fractionally distilled, also in an atmosphere of nitrogen, and a yield of 22 g. (33%) was obtained; b. p. 183–186° at 3 mm. The ester solidified to a white, crystalline mass; after four recrystallizations from petroleum ether it melted at 40.5–41.5°.

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[12] Unpublished communication.

[13] Gilman and others, THIS JOURNAL, 45, 150 (1923).

Anal. Subs., 0.1902: CO_2, 0.4975; H_2O, 0.2026. Calcd. for $C_{17}H_{34}O_3$: C, 71.27; H, 11.97. Found: C, 71.34; H, 11.92.

Several unsuccessful attempts were made to prepare this ester, using methyl 10-aldehydodecanoate which had been worked up and distilled in the ordinary way, that is, with no special precautions to keep the substance absolutely free from acid ester except that it was used immediately after redistillation. In these experiments, the ester obtained from the condensation distilled gradually over a range of 20° (180–200° at 4 mm.) and could not be purified by fractionation; the yield of product was low (18–25%). Upon saponification only about 1 g. of crude acid could be isolated from about 5 g. of ester. Instead of the expected hydroxy acid, the corresponding keto acid was isolated on recrystallization, as was shown by melting point and a mixed melting point with some 11-ketohexadecanoic acid prepared later and described below.

11-Hydroxyhexadecanoic Acid, $CH_3(CH_2)_4CHOH(CH_2)_9CO_2H$.—The methyl 11-hydroxyhexadecanoate was saponified by refluxing for several hours with excess of 10% alcoholic potassium hydroxide. The alcohol was evaporated and the aqueous solution was poured slowly into an excess of hydrochloric acid. The 11-hydroxyhexadecanoic acid was recrystallized four times from ethyl acetate and melted constant at 68–69°.

Anal. Subs., 0.2013: CO_2, 0.5185; H_2O, 0.2125. Calcd. for $C_{16}H_{32}O_3$: C, 70.53; H, 11.84. Found: C, 70.25; H, 11.81.

Mol. wt. Subs., 0.3618: 13.28 cc. of 0.1 *N* NaOH. Calcd. for $C_{16}H_{32}O_3$: mol. wt., 272.3. Found: 272.4.

11-Ketohexadecanoic Acid, $CH_3(CH_2)_4CO(CH_2)_9CO_2H$.—A solution of 0.5 g. of 11-hydroxyhexadecanoic acid in 10–15 cc. of glacial acetic acid was warmed to 50–60°. It was then treated with a solution of 0.5 g. of chromic acid in 2 cc. of water and 8 cc. of glacial acetic acid, kept warm and shaken for four to five minutes, then heated to 60–70° for three to four minutes longer. The solution was poured into a large volume of ice water, the keto acid filtered off and recrystallized from ethyl acetate. Any trace of color, due to chromium, in the keto acid could be readily removed by converting the acid into its sodium salt, heating the aqueous solution of the salt with a small quantity of Norit, filtering and regenerating the acid. After three crystallizations the keto acid melted constant at 74–75' and when mixed with keto acid prepared from jalapinolic acid there was no change in melting point.

Anal. Subs., 0.0981: CO_2, 0.2548; H_2O, 0.0986. Calcd. for $C_{16}H_{30}O_3$: C, 71.06; H, 11.19. Found: C, 70.82; H, 11.24.

11-Hydroxyhexadecanoic Acid Derived from Jalapinolic Acid.—The keto acid from jalapinolic acid was prepared as described above for 11-ketohexadecanoic acid. It was recrystallized to constant melting point, 74–75°. One gram of the keto acid was dissolved in about 20 cc. of ethyl acetate and shaken for ten hours with hydrogen in the presence of about 0.1 *g.* of platinum-oxide platinum black prepared according to the method of Adams and Shriner.[14] The solution was filtered from the catalyst, part of the solvent removed by evaporation and the remainder of the solution cooled, whereupon the hydroxy acid crystallized out. On recrystallization from ethyl acetate it melted at 68–69" and was shown by mixed melting point to be identical with the synthetic 11-hydroxyhexadecanoic acid described above. In one or two instances a second addition of catalyst was required before the reduction was accomplished. In still another instance the reduction yielded a product difficult to purify. This may have been due to the presence of small amounts of acid in which the keto was reduced to a methylene group.

Methyl **11-Hydroxypentadecanoate**, $CH_3(CH_2)_3CHOH(CH_2)_9CO_2CH_3$.—This ester

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[14] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

was prepared by condensing methyl 10-aldehydodecanoate with n-butyl magnesium bromide under the same conditions as described for the corresponding hexadecanoate. It distilled at 166° at 2 mm., solidified on cooling to white crystals which melted at about 29-32°.

Anal. Subs., 0.1847: CO_2, 0.4786; H_2O, 0.1959. Calcd. for $C_{16}H_{32}O_3$: C, 70.53; H, 11.84. Found: C, 70.66; H, 11.87.

The same difficulty was encountered in the synthesis of this ester as in the case of the corresponding hexadecanoate. 'The ester distilled at 170-190° at 3 mm. and the keto acid, instead of the expected hydroxy acid, was obtained from the earlier experiments. This was shown by melting point and by mixed melting point with 11-ketopentadecanoic acid, which is described below.

11-Hydroxypentadecanoic Acid, $CH_3(CH_2)_3CHOH(CH_2)_9CO_2H$.—This acid was prepared by saponification of the corresponding ester. It was recrystallized four times from ethyl acetate and melted at 63.5-64°.

Anal. Subs., 0.1543: CO_2, 0.3926; H_2O, 0.1591. Calcd. for $C_{15}H_{30}O_3$: C, 69.70; H, 11.71. Found: C, 69.40; H, 11.53.

Mol. wt. Subs., 0.3563: 13.80 cc. of 0.1 N NaOH. Calcd. for $C_{15}H_{30}O_3$: mol. wt., 258.2. Found: 258.1.

11-Ketopentadecanoic Acid, $CH_3(CH_2)_3CO(CH_2)_9CO_2H$.—This acid was prepared by oxidation of the corresponding hydroxy acid in the same manner as described for 11-ketohexadecanoic acid. Upon recrystallization to constant melting point from ethyl acetate, it melted at 70-71°. Mixed with a sample of keto acid, m. p. 63°, prepared from convolvulinolic acid, there was a marked depression of the latter melting point.

Anal. Subs., 0.1882: CO_2, 0.4838; H_2O, 0.1830. Calcd. for $C_{15}H_{28}O_3$: C, 70.28; H, 11.01. Found: C, 70.08; H, 10.87.

11-Hydroxypentadecanoic Acid Derived from Convolvulinolic Acid.—A sample of keto acid prepared by the oxidation of convolvulinolic acid was reduced catalytically to the hydroxy acid. The latter was recrystallized from ethyl acetate and melted at 51-52°. This melting point and a mixed melting point proved it to be different from the synthetic 11-hydroxypentadecanoic acid described above. The quantity of convolvulinolic acid available was small; the hydroxy acid obtained from the reduction was sufficient for three crystallizations, but after this treatment was insufficient for analysis. The melting point reported may be considered as approximately correct.

9-Ketohexadecanoic Acid, $CH_3(CH_2)_6CO(CH_2)_7CO_2H$.—Monomethyl azelate was prepared by the ozonation of methyl oleate and decomposition of the ozonide in the presence of hydrogen peroxide. The ester has been described by Noller and Adams.[11a] It was then converted into monomethyl azelayl chloride by the method of Robinson and Robinson;[15] the acid chloride distilled at 139-141° at 4.5 mm. The methyl ester of 9-ketohexadecanoic acid was prepared from monomethyl azelayl chloride and n-heptyl magnesium bromide by a procedure similar to the condensations of aldehyde esters with Grignard reagents previously described. The method is that of John R. Johnson.[12] The methyl ester was saponified and the keto acid, on recrystallization from ethyl acetate, melted at 73.5-74.5°.

Anal. Subs., 0.1857: CO_2, 0.4851; H_2O, 0.1858. Calcd for $C_{16}H_{30}O_3$: C, 71.06; H, 11.19. Found: C, 71.24; H, 11.19.

Mol. wt. Subs., 0.4213: 15.62 cc. of 0.1 N NaOH. Calcd. for $C_{16}H_{30}O_3$: mol. wt., 270.3. Found: 269.9.

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[15] Robinson and Robinson. J. *Chem. Soc.*, 127, 175 (1925).

Summary

1. 11-Hydroxyhexadecanoic acid and 11-hydroxypentadecanoic acid have been synthesized by the condensation of methyl 10-aldehydodecanoate with n-amyl magnesium bromide and n-butyl magnesium bromide, respectively, and subsequent saponification of the esters obtained.

2. Jalapinolic acid has been shown to be the d-form of 11-hydroxyhexadecanoic acid. This has been accomplished through oxidation of both substances to the same keto acid, and also by the reduction of the keto acid derived from jalapinolic acid to a substance identical with the synthetic 11-hydroxyhexadecanoic acid.

3. Convolvulinolic acid has been shown to have a structure different from that of 11-hydroxypentadecanoic acid. The procedure used in investigating this substance was identical with that used in the study of jalapinolic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND THE BAKER CHEMICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF SULFONEFLUORESCEIN AND SOME OF ITS DERIVATIVES[1]

BY R. C. GIBBS AND C. V. SHAPIRO[2]

RECEIVED MARCH 12, 1928 PUBLISHED JUNE 5, 1928

Sulfonefluorescein[3] is a sulfonic acid derivative of resorcinolbenzein and is analogous in many of its chemical properties to fluorescein. The absorption spectra of resorcinolbenzein[4a] and fluorescein[4b] have already been investigated in this Laboratory. All of the substances used in this study were analytically pure samples prepared by Dr. Vose.[3]

Fig. 1 gives the absorption spectra of neutral alcoholic solutions of sulfonefluorescein, dibromosulfonefluorescein and 2,4-dihydroxybenzoylbenzene-o-sulfonic acid, the intermediate product in the formation of sulfonefluorescein from resorcinol and o-sulfobenzoic acid anhydride. The absorption of 2,4-dihydroxybenzoylbenzene-*o*-sulfonic acid, Curve C, is characterized by three absorption bands and is entirely similar to the absorption of 2,4-dihydroxybenzoyl-*o*-benzoic acid,[4b] the bands for the former being shifted slightly toward higher frequency numbers. The structure of these intermediate acids has been the subject of considerable

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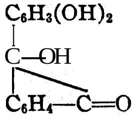
[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Heckscher Research Assistant in Physics and Chemistry, Cornell University, 1923–1928.

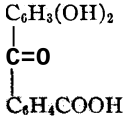
[3] Orndorff and Vose, THIS JOURNAL, 46,1896 (1924).

[4] Orndorff, Gibbs and Shapiro, *ibid.*, (a) 48, 1327 (1926); (b) 50, 819 (1928).

debate, Graebe, Kohn and Huguenin[5] assigning to them a lactone form, I, while Heller[6] proposed the ketone structure, II.



I

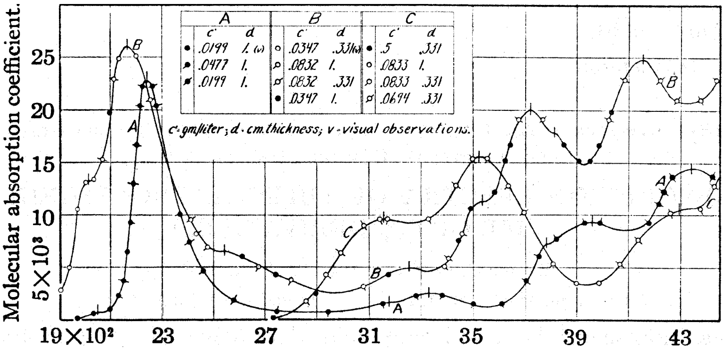


$$\begin{array}{l} C_6H_3(OH)_2 \\ | \\ C{=}O \\ | \\ C_6H_4COOH \end{array}$$

XI

2,4-Dihydroxybenzoyl-*o*-benzoic acid

A comparison of the position of the bands in the absorption spectra of these acids with those of benzoic aldehyde and acetophenone,[7] Table-I, as well as the general similarity in the shape of the curves, shows conclusively that the intermediate acids, in the free state, are to be regarded as ketone derivatives. If they were present in solution in the lactone form, it is to be expected that they would have the same type of absorption spectra as diphenylphthalide and phenolphthalein,[8] but there is no indication of such a relation. As was pointed out above, the tautomeric nature of these acids was early recognized from their chemical behavior but no decisive criterion, such as the present study of absorption spectra, has been applied to determine which form is present in the free state.



Frequency numbers (mm.$^{-1}$)

Fig. 1.—Neutral alcoholic solutions. *A*, sulfonefluorescein; *B*, dibromosulfonefluorescein; *C*, 2,4-dihydroxybenzoylbenzene-*o*-sulfonic acid.

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[5] Graebe, Kohn and Huguenin, *Arch. sci. phys. nat.*, *30*, 91 (1893).

[6] Heller, *Ber.*, 28, 315 (1895). See also Orndorff and collaborators, This Journal, 40, 1239 (1918); 44, 1518 (1922); 46, 2276 (1924).

[7] Bielecki and Henri, Ber., 47, 1690 (1914). The absorption spectrum of benzophenone, the parent substance of the intermediate acids, has the same general outline according to data presented by Scheibe, Ber., 59, 2626 (1926), although Castille, *Bull. Acad. Roy. Belg.*, 12, 498 (1926), has shown that the first band at about frequency number 2900 can be resolved into five narrow bands. This effect is to be correlated with the presence of two unsubstituted phenyl groups in the benzophenone molecule, in contrast with the intermediate acids, in which both phenyl groups are substituted.

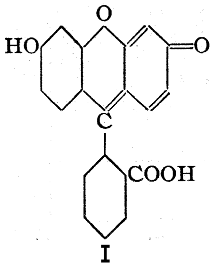
[8] Orndorff, Gibbs and McNulty, This Journal, 48, 1994 (1926).

TABLE I

FREQUENCY NUMBERS OF BANDS IN ALCOHOLIC SOLUTIONS OF:

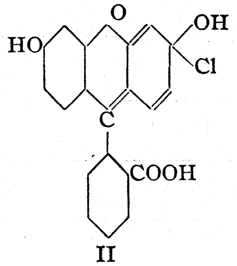
Benzoic aldehyde	Acetophenone	2,4-Dihydroxybenzoyl-a-benzoic acid	2,4-Dihydroxybenzoylbenzene-o-sulfonic acid
3050	3140	3144	3156
3563	3590	3515	3522
4097	4140	4208	4294

Sulfonefluorescein, Curve A, and dibromosulfonefluorescein, Curve B, exhibit fairly similar though displaced spectra. The absorption of these two compounds, however, shows no evident relation to that of either fluorescein or resorcinolbenzein. As was noted in the case of fluorescein,[4b] its resemblance to resorcinolbenzein does not extend beyond the first four bands. In the present case, the two visible bands of sulfonefluorescein are only slightly reminiscent of the two in neutral fluorescein. If we compare, however, the absorption of an alcoholic solution of fluorescein containing hydrogen chloride with that of a *neutral* solution of sulfonefluorescein, the identity of the absorption bands is striking: fluorescein (1 mole: 960 moles HCl), 2258, 3240, 3349, 3790, 4018; sulfonefluorescein (neutral solution), (2050), 2241, 3177, 3328, 3781, 3962, (4340). It is well known that the sulfonic acid group is much more highly ionized in solution than the carboxylic group. Further, sulfonefluorescein does not form a hydrochloride, nor does the addition of hydrogen chloride to a neutral alcoholic solution affect the absorption in the slightest degree, even when the ratio of acid to sulfonefluorescein is as high as 10,000 molecules to one. Sulfonefluorescein must, therefore, be regarded as an inner carbonium salt, III, similar in structure to fluorescein hydrochloride, II, while fluorescein probably exists as the free acid, I.



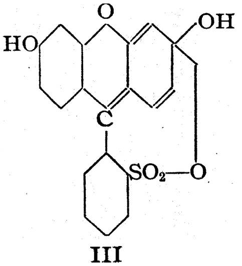
I

Fluorescein



II

Fluorescein hydrochloride



III

Sulfonefluorescein

Dibromosulfonefluorescein is likewise assigned an inner salt structure on the basis of its resemblance to sulfonefluorescein. This assignment appears to be the most satisfactory way to account by means of structural formulas for the similarity of both chemical and optical properties of these compounds.

Orndorff and Vose[3] prepared colored diacetates of both sulfonefluorescein and its dibromo derivative, which dissolve in absolute alcohol to give yellow solutions, but which were, nevertheless, assigned lactoid structures. A study of the absorption spectra of these diacetates, Pig. 2, Curves A and B, not only shows them to be entirely different from the absorption of the corresponding diacetate of fluorescein,[4b] but also brings out a degree

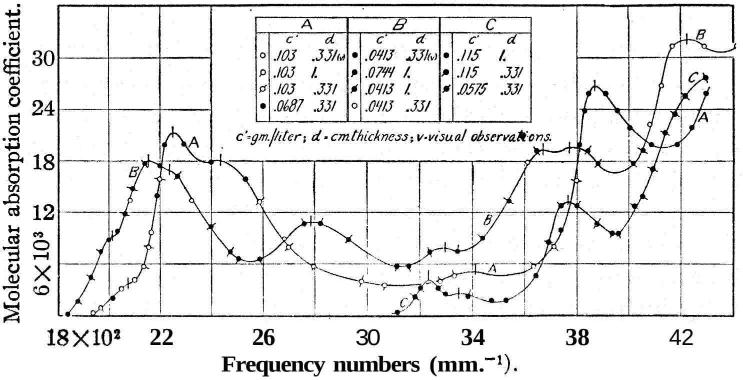


Fig. 2.—Neutral alcoholic solutions. A, sulfonefluorescein diacetate; B, dibromosulfonefluorescein diacetate; C, 3,3′-dichlorosulfonefluoran.

of similarity with neutral sulfonefluorescein. We are inclined, therefore, to regard the diacetates as possessing a quinoid structure which is derived directly from the inner carbonium salt structure of sulfonefluorescein. This would account for the high color of the compounds and for the relative

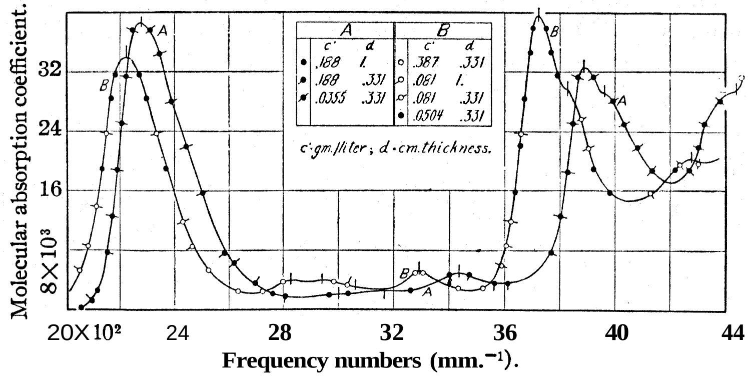


Fig. 3.—Concentrated sulfuric acid solutions. A, sulfonefluorescein; B, dibromosulfonefluorescein.

complexity of the absorption spectra. On the other hand, sulfonefluorescein dichloride or, more correctly, 3,3′-dichlorosulfonefluoran, which can only be assigned a lactoid structure, is a colorless compound and exhibits an absorption, Curve C, more nearly resembling that of the lactoid derivatives of fluorescein.

Sulfonefluorescein and dibromosulfonefluorescein dissolve in concentrated sulfuric acid to give yellow solutions having a pronounced green fluorescence. The absorption of these solutions, Fig. 3, Curves A and B, is typical of all compounds structurally related to fluorescein thus far examined in concentrated sulfuric acid. The absorption spectrum always contains a prominent band in the blue or violet, a series of weak bands in the middle ultraviolet and a prominent double or complex band in the further ultraviolet. These are followed in the present case by a band in the extreme ultraviolet region, but if such a band were present in resorcinolbenzein or fluorescein, calculation shows that it would lie just beyond the range of our spectrograph. A band similar to this last one has also been located in sulfuric acid solutions of dibromo- and tetrabromofluorescein.[9] The remarkable resemblance of the absorption curves for these various compounds in sulfuric acid solution and the consistent confirmation of Hartley's rule, that increase in molecular weight shifts the band toward longer wave lengths, is well brought out in Part A, Fig. 4.

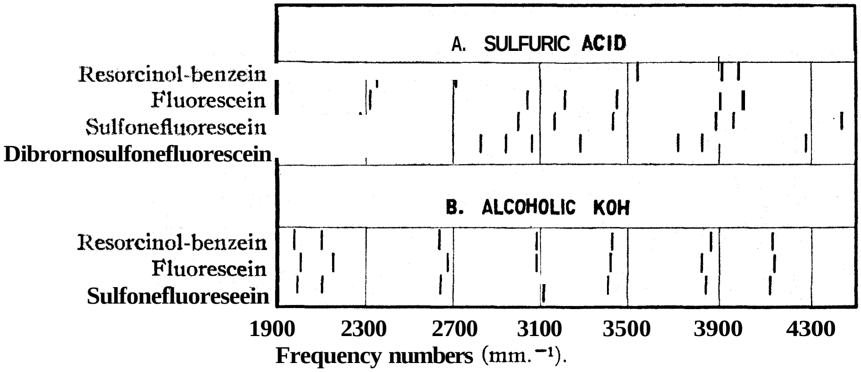


Fig. 4.—Relative positions of absorption bands in acid and alkaline solutions of some fluoresceins.

Fig. 5 shows the absorption of alcoholic solutions of sulfonefluorescein containing varying amounts of potassium hydroxide. Curve A, A', for one molecule of potassium hydroxide to one of sulfonefluorescein shows bands characteristic of both the neutral and alkaline states. The two bands of Curve A are entirely comparable with the first two bands in a neutral solution of fluorescein. There is, apparently, sufficient alkali present to break the inner carbonium salt bond of the neutral sulfonefluorescein and set free the acid, but not enough to bring out the prominent band at 1990 which is characteristic of the alkali salt. Increasing the ratio of alkali to 4 and 25 molecules, Curves B, B' and C, C', respectively,

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[9] Unpublished data.

brings out the distinctive absorption of the alkali salt and, as can be seen from B, Fig. 4, this absorption is practically identical with that of the alkali salts of resorcinolbenzein and fluorescein. It is significant in this connection that the acid and basic salts of the various derivatives of resorcinolbenzein considered thus far give uniform types of absorption, whereas the neutral solutions show decided variations. While these variations are primarily due to the specific chemical properties of the added substituent groups, such as carboxyl and sulfoxyl and hence are less susceptible of expression in a rigid structural formula, the spectroscopic evidence in this case justifies the use of different structures for fluorescein and sulfonefluorescein. On the other hand, the presence of external forces, such as strong acid or basic solutions, can overcome these individual differences and produce a uniformity of structure, as is made evident by the striking similarity in the absorption spectra of these salts.

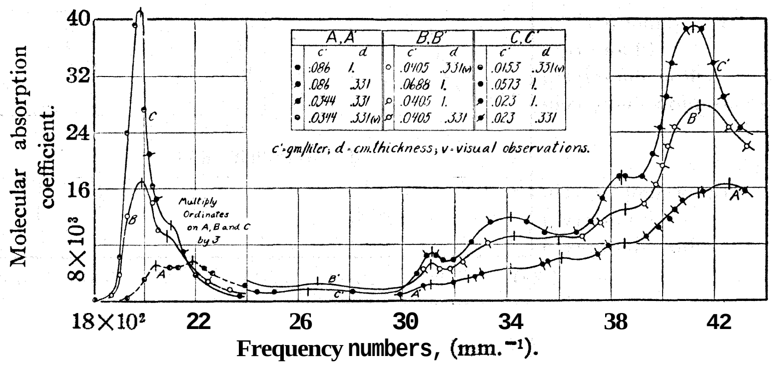

Fig. 5.—Sulfonefluorescein in alcoholic KOH. A, 1 molecule: 1 molecule KOH; *B*, 1 molecule: 4 molecules KOH; *C*, 1 molecule: 25 molecules KOH.

When dissolved in 33% aqueous potassium hydroxide, sulfonefluorescein yields an orange-colored solution with an intense green fluorescence. On standing for several days, the color gradually changes to purple with an evident decrease in intensity. As in the case of fluorescein,[11] the production of the purple color can be hastened, either by heating the alkaline solution or by dissolving the solid potassium hydroxide and sulfonefluorescein in water simultaneously. The absorption of solutions prepared in both ways is shown in Fig. 6. Curve A, A' for a freshly prepared cold solution, Curve B, B' for the same solution two weeks later and Curve C, C' for a freshly prepared hot solution, examined after twelve hours to allow for cooling, all show the same general type of absorption. This again emphasizes the point that was made in discussing the behavior of fluorescein under like conditions, namely, that the rupture of the pyrone ring, to which Baeyer ascribed the change in color from orange to purple, has no radical effect on the absorption of the solution, except for the growth of an existent band at frequency number 1740. However, the breaking of the pyrone ring with the accompanying formation of a tetrabasic salt is followed by a gradual disruption of the molecule, as indicated by the decrease in intensity of the bands at 1740 and 1997. After eight months the solution had faded to a pale pink, and the absorption in the ultraviolet region, Curve D′, had changed completely in character. This slow fading of the solution is not due to carbinol formation entirely, for the original color of the fresh solution cannot be restored by dilution with water, after the process has gone on for some time, nor can the fluorescein or sulfonefluorescein be reprecipitated by acidification, as is possible with faded solutions of the phthaleins. It appears, rather, that after the pyrone ring is broken the molecule is disrupted, with the formation of decomposition products whose identity has not yet been established.

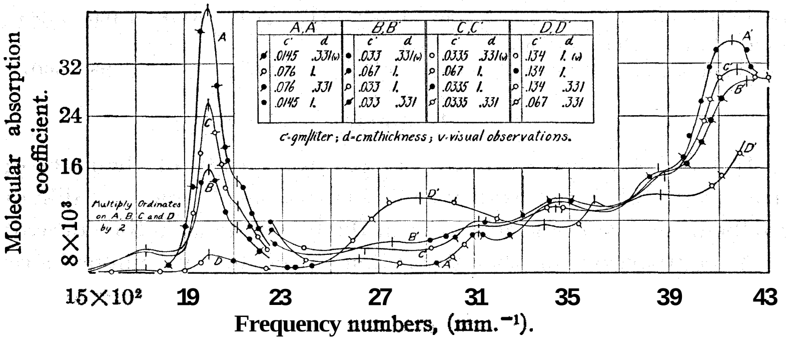

Fig. 6.—**Sulfonefluorescein in 33% aqueous KOH: A, freshly prepared, cold solution; *B*, solution "A," after two weeks; *C*, hot solution, after twelve hours; D, solution "C," after 8 months.**

Table II summarizes the positions of the absorption bands in the various solutions of sulfonefluorescein and its derivatives.

TABLE II

FREQUENCY NUMBERS OF ABSORPTION BANDS

ABSOLUTE ALCOHOL SOLUTION

2,4-Dihydroxybenzoylbenzene-*o*-sulfonic acid				3156		3522		4294
Sulfonefluorescein	2050	2241		3177	3328	3781	3962	4340
Dibromosulfonefluorescein	2010	2165	2543	3253	3535	3720	3813	4154
Sulfonefluoresceindiacetate	2075	2250	2436		3411		3868	
Dibromosulfonefluoresceindiacetate	2013	2155	2236	2786	3297	3671	3770	4223
Sulfonefluorescein dichloride					3233	3348	3765	

CONCENTRATED SULFURIC ACID SOLUTION

Sulfonefluorescein	2279		3001	3265	3436	3885	3961	4435
Dibromosulfonefluorescein	2224	2828	2942	3062	3291	3721	3826	4278

TABLE II (*Concluded*)

ALCOHOLIC POTASSIUM HYDROXIDE SOLUTION

Sulfonefluorescein (1 mole):1 mole of potassium hydroxide	2045	2188	2665	3110	3252	3414	3609	3853	4139	4260
Sulfonefluorescein (1 mole):4 moles of potasium hydroxide			1990	2088	2676	3109	3427	3598	3856	4145
Sulfonefluorescein (1 mole):25 moles of potassium hydroxide			1990	2104	2639	3113	3415		3841	4120

33% AQUEOUS POTASSIUM HYDROXIDE SOLUTION

Sulfonefluorescein, freshly prepared cold solution	1740	1997	2114	2618	3118	3460	3861	4165
Solution above after standing for two weeks	1740	1997	2114	2757	3118	3445	3885	4215
Freshly prepared hot solution after twelve hours	1740	1997	2117	2642	3118	3460	3885	4175
Solution above after standing for eight months	1740	1997		2873		3398	3601	3869

Summary

1. It has been shown from a comparative study of their absorption spectra that 2,4-dihydroxybenzoyl-*o*-benzoic acid and **2,4-dihydroxybenzoylbenzene-o-sulfonic** acid exist in the free state as ketone derivatives.

2. **A** comparison of the absorption spectrum of sulfonefluorescein in neutral alcoholic solution with that of fluorescein in neutral and acid solution has led to the suggestion that sulfonefluorescein has an inner salt structure.

3. The absorption spectra of sulfonefluorescein in concentrated sulfuric acid solution and in alcoholic alkaline solution bear a close relationship to the spectra of resorcinolbenzein and fluorescein in the same solvents.

4. The absorption of sulfonefluorescein in strong, aqueous potassium hydroxide changes progressively, indicating two successive chemical changes: (1) the breaking of the pyrone ring and (2) the probable disruption of the molecule.

ITHACA, NEW YORK

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

DERIVATIVES OF NORMAL BUTYLBENZENE[1]

BY R. R. READ AND D. B. MULLIN

RECEIVED MARCH 14, 1928 PUBLISHED JUNE 5, 1928

During a study of the effect on the disinfectant power of phenol of various groups in the three isomeric positions on the ring it was necessary to prepare a number of derivatives of n-butylbenzene as intermediates in the preparation of the three n-butylphenols.

Preliminary examination of these phenols[2] has shown that they have a high phenol coefficient and also that there was an apparent difference in the coefficients, the activity decreasing in the order meta, *ortho*, *para*. Later, more detailed examination[3] has shown that factors not taken into consideration during the preliminary tests influence these values so markedly that the order given above cannot be considered as valid.

A later paper will deal with this problem.

Johnson and Lane have pointed out[4] that in the case of methyl-, ethyl-, n-propyl-, and n-butylresorcinol the disinfectant power is a function of the weight of the side chain. More recently Leonard[5] reported that this holds only up through the hexyl group and that certain branched chains are less effective than the corresponding normal chains. In a later paper it will be shown that other factors are of even greater influence than weight in determining the disinfectant power of a phenol.

Experimental Part

Normal butylbenzene was prepared by the condensation of n-butyl bromide and bromobenzene with sodium.[6]

Nitration.—Five hundred g. of butylbenzene was added slowly to 500 g. of concd. sulfuric acid at 0°. To this mixture was added with stirring the nitrating acid (375 g. of concd. nitric acid and 787 g. of concd. sulfuric acid) over a period of five hours at 5–12'. External cooling was necessary. After 30 minutes at this temperature the emulsion was poured over 1.5 kg. of ice. The oil was removed and the aqueous portion extracted with benzene, the combined material washed with carbonate solution and dried over sodium sulfate. The removal of the benzene completed the drying.

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[1] The field of the effect of hydrocarbon side chains on the disinfectant power of phenols was opened by Johnson and Lane and it is to these investigators that the writers are indebted for the opening of the field to them. A preliminary version of this manuscript was submitted on September 21, 1925, but publication was withheld by request.

[2] The writers are indebted to Professor B. F. Lutman of this University for this examination.

[3] A bacteriological study involving the use of these phenols is now being made by Professor L. F. Rettger of Yale University.

[4] Johnson and Lane, THIS JOURNAL, 43,348 (1921).

[5] Leonard, J. *Urol.*, 12,585 (1924).

[6] Read and Foster, THIS JOURNAL, 48, 1606 (1926).

Fractionation through a jacketed Clarke-Rahrs column gave a fore run of butylbenzene, then **(1)** a fraction boiling at 131–133° (15 mm.), followed by a small intermediate fraction at 133–143° (15 mm.), then **(2)** a fraction boiling at 143–145° (15 mm,). Fraction **1** yielded on oxidation an acid melting at 146°, and was therefore o-nitro-*n*-butylbenzene; d_4^{20}, **1.071.**

Anal. Subs. **0.4281, 0.4129: 24.45** cc., **23.80** cc. of **0.01106** N acid. Calcd. for $C_{10}H_{13}NO_2$: N, **7.8. Found: 7.2, 7.3.**

Fraction **2** yielded on oxidation an acid melting at 238–240°, and was, therefore *p*-nitro-*n*-butylbenzene; d_4^{20}, **1.065.**

Anal. Subs., **0.4006, 0.4074: 23.1** cc., **24.2** cc. of **0.01106** N acid. Calcd. for $C_{10}H_{13}NO_2$: N, **7.8.** Found: **7.3, 7.5.**

Nitration of the butylbenzene in glacial acetic acid with fuming nitric acid dissolved in glacial acetic acid (in the ratio **1:1:2:1)** at 10° gave a 70% yield of the *para* compound with only very small amounts of the *ortho.*

Reduction.—The reduction was carried out by the usual procedure with tin and hydrochloric acid, and the product recovered by benzene extraction of the alkaline sludge, steam vacuum distillation of the extract, and distillation through a jacketed Clarke-Rahrs column. Ordinary steam distillation can be used in place of the extraction and steam vacuum distillation but the amine comes over very slowly.

o-n-Butylaniline; b. p. 122–125° (12 mm.); d_4^{20}, **0.953.**

Anal. Subs., **0.1556, 0.1626: 11.8** cc., **12.5** cc. of **0.01106** *N* acid. Calcd. for $C_{10}H_{15}N$: N, **9.4. Found: 9.6, 9.7.**

The hydrochloride was prepared, crystallizing from benzene as white scales; m. p. **137°.**

Anal. Subs., **0.1462, 0.1504: AgCl, 0.1136, 0.1171.** Calcd. for $C_{10}H_{16}ClN$: **Cl, 19.12.** Found: **19.22. 19.26.**

p-n-Butylaniline; b. p. 133–134° (**14** mm.); d_4^{20}, **0.945.** This compound has been prepared previously[7] but its boiling point under reduced pressure was not recorded.

Replacement of Amino by Hydroxyl Group.—This was accomplished by the usual procedure of diazotization of the sulfate of the amine and slow elevation of the temperature to 60°. The phenol was extracted with benzene, and purified through the sodium salt which forms intensely red solutions in water.

p-n-Butylphenol; b. p. 121–123° (**9** mm.); 746–750° (**751** mm.), d_4^{20}, **0.978.** This compound has been described previously.[7] The *p*-nitrobenzoate crystallizes in yellow needles from alcohol; m. p. 67–68°.

Anal. Subs., **0.3160:** 12.0 cc. of **0.01106** ***N* acid.** Calcd. for $C_{17}H_{17}NO_4$: N, **4.7:** Found: **4.9.**

o-n-Butylphenol; b. p. 113–115° (**14** mm.); 234–237° (**760** mm.); d_4^{20}, **0.975.**

Anal. Subs., **0.1890:** CO_2, **0.5532;** H_2O, **0.1566.** Calcd for $C_{10}H_{14}O$: C, **80.0; H, 9.3.** Found: **C, 79.8;** H, **9.2.**

m-n-Butylphenol.—*p*-Butylaniline was acetylated with glacial acetic acid and crystallized from benzene-petroleum ether; m. p. 104°, corresponding with that found by Reilly and Hickenbottom, This anilide was nitrated[8] and the nitro derivative (2-nitro-4-n-butylacetanilide) crystallized from 50% alcohol as fine, yellow needles in radiating clusters.

Anal. Subs., **0.1560: 14.3** cc. of **0.01106** *N* acid. Calcd. for $C_{12}H_{16}N_2O_3$: N, **11.9.** Found: **11.6.**

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[7] Reilly and Hickenbottom, J. *Chem. Soc.*, 117, **103 (1920).**

[8] Noyes, "Organic Chemistry," H. Holt and Company, New York, 1903.

The nitro-anilide was hydrolyzed in alcoholic potassium hydroxide from which water precipitated the 2-nitro-4-n-butylaniline. The amino group was removed by the reduction of the diazonium sulfate[9] and the resulting m-nitro-n-butylbenzene reduced as previously noted; b. p., 133° (18 mm.). The melting point of its benzoate (67–68°) checked that previously recorded (68°).

The phenol, m-n-butylphenol, was prepared and purified as in the case of the other isomers; b. p. 247–249° (758 mm.); d_4^{20}, 0.974.

Anal. Subs., 0.1853: CO_2, 0.5397; H_2O, 0.1554. Calcd. for $C_{10}H_{14}O$: C, 80 0; H, 9.3. Found C, 79.4; H, 9.3.

Summary

Various derivatives of n-butylbenzene have been synthesized including the three isomeric phenols. The phenols are powerful disinfectants.

BURLINGTON, VERMONT

[CONTRIBUTION FROM THE LABORATORIES OF THE MONSANTO CHEMICAL WORKS]

THE PHYSICAL PROPERTIES OF SALICYLALDEHYDE

BY T. S. CARSWELL AND C. E. PFEIFER

RECEIVED MARCH 14, 1928 PUBLISHED JUNE 5, 1928

In connection with some work on salicylaldehyde, the writers recently had occasion to prepare a highly purified sample of this material. We found that the physical properties were quite different from those given in the most recent literature and for this reason our results are reported here in detail.

As is frequently the case with compounds of this nature, the data given in the literature are quite conflicting. Walden[1] gives the crystallizing points as −10 to −11°, and in a later publication the density is given as $d_{4°}^{25°} = 1.15390$. Perkin[2] gives the boiling point under 760 mm. as 197° (corr.), and the density at 20° as 1.1495. Jaeger[3] purified the commercial aldehyde by fractionation, and obtained a boiling point of 192.5°, crystallizing point of −7° and density as $d_{4°}^{25°} = 1.1525$. The International Critical Tables (1926) give the melting point as −7°, the boiling point as 196.5" and the density as 1.167.

In preparing our purified product we started with a commercial sample of aldehyde, which already had a crystallizing point of −7°. This material was carefully fractionated in vacuum, using a column about four feet long packed with 1/8-inch Raschig rings. The middle fraction of the aldehyde obtained by this fractionation had a crystallizing point of 1°. This fraction was further purified by the following treatment.

Three hundred g. of the fraction with 1° crystallizing point was slowly

[9] Bigelow, THIS JOURNAL, 41, 1559 (1919).

[1] Walden, *Z. physik. Chem.*, 55, 220 (1906).

[2] Perkin, *J. Chem. Soc.*, *68*, 1200 (1895).

[3] Jaeger, *Z. anorg. allgem. Chem.*, 101, 142 (1917).

added, with agitation, to an alcoholic solution of sodium bisulfite. A slight excess of bisulfite was used. In a short time a voluminous yellow precipitate of the bisulfite compound separated. The precipitate was filtered off and washed with alcohol and ether, after which it became nearly white in color. The precipitate was then recrystallized once from 10% alcohol, after which the bisulfite compound was obtained as pure white crystals.

An attempt was made to hydrolyze the bisulfite compound with sodium carbonate. However, when the bisulfite compound was mixed with sodium carbonate solution, an abundant yellowish-white precipitate was formed. This precipitate was filtered off, sludged up with water and treated with hydrochloric acid until acid to congo red. There was considerable effervescence and the aldehyde separated as a yellowish oil. The oil was fractionated under vacuum and the middle fraction was refractionated under atmospheric pressure.

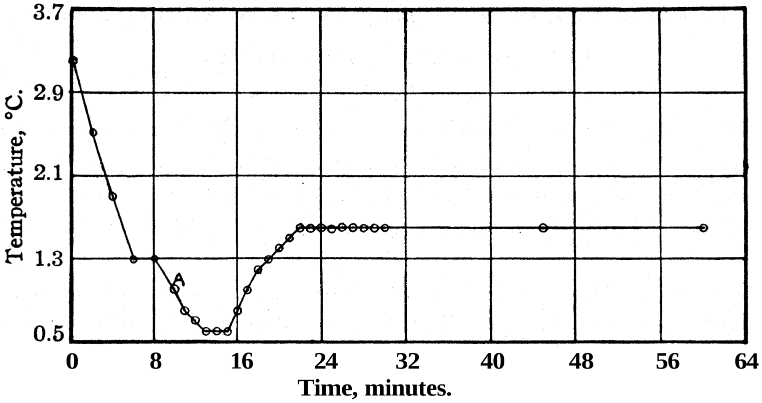

Fig. 1.--Cooling curve of salicylaldehyde (seeded at A).

The purified product so obtained had the following properties: boiling point under 751 mm., 196.4–196.5°; boiling point under 25 mm., 93°; crystallizing point, 1.6°; $d_{20°}^{20°}$ = 1.1690. The temperatures were measured with thermometers calibrated by the Bureau of Standards and the density was taken in a bottle type pycnometer.

The crystallizing point was determined by slowly cooling 30 g. of the product and observing the temperature as crystallization proceeded. To prevent excessive supercooling, the sample was seeded when the temperature was about 1° below the crystallizing point. The time–temperature data are given in Fig. 1.

The constancy of the crystallizing point as crystallization proceeded shows that our preparation was quite pure.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OR MINNESOTA]

CONTROL OF THE MOLECULAR WEIGHT OF LIQUID HYDROCARBONS PRODUCED BY ELECTRICAL DISCHARGE IN ETHANE[1]

BY S. C. LIND[2] AND GEORGE GLOCKLER[3]

RECEIVED MARCH 15, 1928 PUBLISHED JUNE 5, 1928

In a recent paper[4] we described the production of a heavy oil obtained, besides various gaseous products, from ethane under the influence of silent electrical discharge in an ozonizer type of discharge tube.

The great viscosity and high average molecular weight (467 by freezing point in benzene) of the oil obtained as a direct product of ethane were notable. According to the original theory[5] for the ionizing effect of a-rays on hydrocarbons, there are two ways in which the lower saturated hydrocarbons may be condensed to liquid by ionization: (1) by repeated doubling by means of *successive* ionization until a product is obtained of sufficiently high molecular weight to condense as liquid or (2) by direct condensation of a sufficiently large number of "nascent unsaturates" (those with only one of the double bonds closed) to form liquid directly without repeated ionization.

That the chemical action of a-particles on paraffins is not confined to the gaseous members has been shown in several instances. Lind and Bardwell[6] showed that propane yields a liquid under a low intensity of radiation, but that the liquid is transformed to solid upon prolonged radiation. Rutherford and Boltwood[7] found that solid paraffin exposed to a-rays had its melting point greatly raised, accompanied by an evolution of much gas. W. T. Richards[8] has recently shown that a gas (principally hydrogen) is evolved under a-radiation from both liquid and solid paraffins. Lind[9] has calculated from Richards' results that the quantity of gas per ion-pair is approximately the same as for the gaseous members.

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[1] This paper includes part of an investigation of "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," Project No. 8 of American Petroleum Institute Research. Financial assistance has been received from the research fund of the American Petroleum Institute, donated by the Universal Oil Products Company. This fund is administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 8.

[3] American Petroleum Institute Research Associate.

[4] S. C. Lind and Geo. Glockler, *Tr. Am. Electrochenr. Soc.*, Vol. *52,* Preprint No. 6, September, 1927.

[5] S. C. Lind and D. C. Bardwell, THIS JOURNAL, **48,** 2331 (1926).

[6] Ref. 5, p. 2341.

[7] Rutherford and Boltwood, *Science,* 60, 364 (1924).

[8] W. T. Richards, *Proc. Camb. Phil. Soc., 23,* 516–522 (1927).

[9] S. C. Lind, "Chemical Effects of Alpha Particles and Electrons," 2d ed., Chemical Catalog Co., New York, 1928, p. 150.

Therefore, if the theory proposed for the a-ray condensation is valid for electrical discharge, we should expect that the first liquid droplets deposited on the wall of the discharge tube would be subject to much secondary electronic bombardment, since the discharge in an ozonizer enters the gas space entirely through the wall. If then by warming the wall we can prevent liquid from condensing there, and if by putting a low temperature trap in the circuit we stop the earlier condensation products from returning to the region of discharge, we may expect a ma-

TABLE I

PRODUCTION OF CONDENSATES OF LOW MOLECULAR WEIGHT

Variables—Types of discharge, temperature of electrodes and temperature of condensation traps.

Oil	Type of discharge tube used[a]	Volts	Milli-amps.[b]	Temp. of electrodes,[c] °C.	Temp. of traps,[d] °C.	Mol. wt. of liquid mixture	n^{20}_{Sun}	Color of liquid	Yield liquid product, cc./hour
1	Ozonizer	11600	<1	25	25	467	1.4900	Red-brown	0.028
2	Ozonizer	11600	<1	70	25	188	1.4642	Slightly yellow	.011
3	Ozonizer	11600	<1	70	−50	184	1.4509	Slightly yellow	,006
4	Semi-Pt wire corona	11600	<1	70	−50	156	1.4467	Slightly yellow	063
5–6	Semi Al rod corona	11600	<1	18	−50	106"	1.4.503	Slightly yellow	.100
7	Semi Al rod corona	11600	<1	70	−50	105[f]	1.4294	Yellow	.100
8	Semi Al rod corona	3000 (Radio)	135	70	−50	95[g]	....	Red-yellow	.060
9	Semi Al rod corona	10000 (Radio)	700	35	−50	109	1.4204	Light yellow	.100
10	Al tube–Pt wire corona	8000	<1	...	−58	81 and 182[h]	....	Red-yellow	.050

[a] For details of construction see below.

[b] See paragraph on electrical energy.

[c] In runs **1** to **3** the inner and outer water electrodes were kept at the temperature indicated; in Expts. **4** to **9** the temperature refers to the outer water electrode.

[d] In Expts. **1** to **4** one condensation trap was used. In runs **5** to **8** two traps were used in series. In 9 and **10** four traps were used in series.

[e] Oil No. 5 (mol. wt. 112) was collected in the first trap and oil No. 6 (mol. wt. 100) was collected in the next trap. The molecular weight indicated is the average.

[f] The molecular weight indicated is the average of the liquid collected in the two traps.

[g] The molecular weight indicated is of the lighter fraction obtained from the total mixture by low temperature vacuum distillation into two equal fractions. The heavier fraction was too insoluble in benzene for molecular weight determination.

[h] The total yield of the four traps was separated by vacuum distillation into two nearly equal fractions and their molecular weights are as given.

terial reduction in the degree of condensation or doubling of the liquid product, which will be manifest in a lowering of its molecular weight. The results in Table I demonstrate the truth of these predictions.

Types of Discharge Vessel Used.—Four different types of tubes have been used. The ordinary all-glass Siemens ozonizer with inner and outer electrode consisting of water jackets filled with tap water is shown in Fig. 1(I). The inner glass tube has an outer diameter of 2.26 cm. and the glass wall is 0.1 cm. thick. The outer glass tube has an inner diameter of 2.6 cm. and is 0.15 cm. thick. The annular space between the glass walls is 0.17 cm. The semi-wire corona tube shown in Fig. 1(II) has a central platinum wire 0.0324 cm. in diameter fastened in a glass tube of 1.85 cm. inside diameter and of 0.075 cm. wall thickness. Fig. 1(III) shows an aluminum rod semi-corona. The aluminum rod is 0.32 cm. in diameter and is located in the center of a glass tube which is 1.3 cm. in inside diameter and of 0.07 cm. wall thickness. The corona tube shown in Fig. 1(IV) consists of an aluminum tube 2.25 cm. in inside diameter with a platinum wire 0.0324 cm. in diameter fastened centrally.

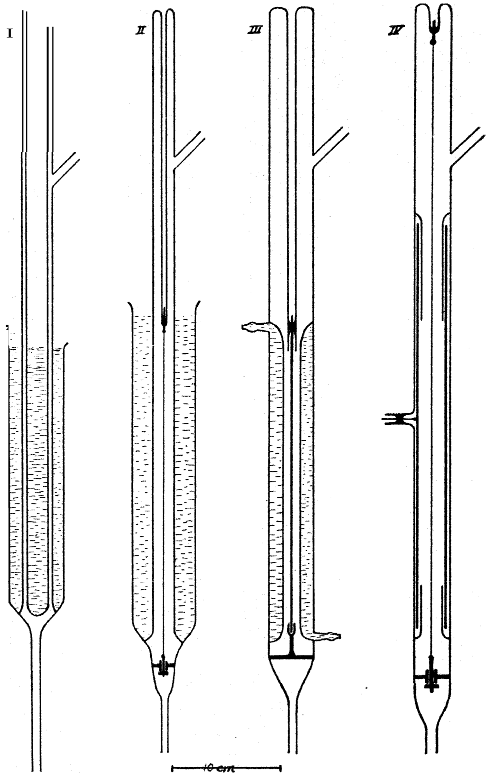

Fig. 1.

The Reaction Vessel.—The Circulating System was the same as described in the previous paper[4] except that the improved horizontal pump[10] utilizing both strokes was employed on account of its higher capacity. The reaction system is shown in Fig. 2. The set of four condensation traps shown there was finally adopted in Expts. 9 and 10 in order to condense all of the reaction products. The traps had spiral inlet tubes which were immersed in a paste of petroleum and aluminum powder contained in solid aluminum blocks which could be kept cool by spraying liquid air into a hole in the block. Pentane thermometers were used to measure the temperature. It was not difficult to maintain −50° within a degree.

Electrical Energy Used.—We have not been able to make satisfactory current measurements in the secondary current circuit. As electrical leakage was reduced by improving the discharge tubes, the readings in the hot wire milli-ammeter were di-

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[10] W. S. Funnell and G. I. Hoover, J. Phys. *Chem.*, **31, 1099 (1927).**

minished until it was evident that certainly less than a milli-ampere flowed through the reaction vessel. In Expt. **8** the reaction vessel was placed in the secondary of a Tesla transformer which was fed from an oscillating circuit containing condenser **(0.0018** microfarad) and rotating spark gap. In Expt. **9** the reaction vessel was placed in the oscillating circuit itself. It is seen that the currents flowing were then very large but the chemical reaction produced was not augmented thereby. These large currents do not cross the reaction space as conduction currents, they only serve to charge the reaction vessel (as an electrical condenser) and do not contribute to the ionization in the gas space on which the chemical reaction is believed to depend,

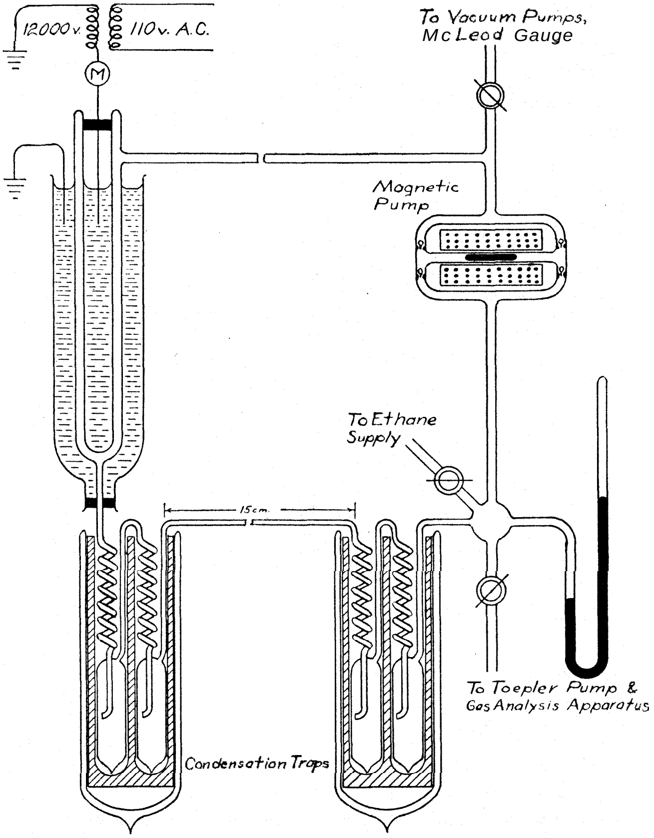

Fig. 2.

Discussion

The type of discharge employed does not seem to influence the reaction products greatly.[11] This would be expected if ionization is the primary

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[11] If the results with electrodes at 70° and the traps at −50° be considered separately, there do appear to be some consistent differences in average molecular weight for the different types of discharge. It is to be remembered, however, that even at 70° liquid product flows down the walls rather slowly and the slower the less liquid is formed

step. Some secondary differences, however, were found. In the semi-corona and corona discharges (Expts. 4 to 10, Table I) there was some cracking to give free carbon, and always in corona there is formation of a solid film on the wall, which peels off readily in a coherent skin that rolls into small hollow cylinders when removed. This solid burns easily but is inert toward solvents—unlike the liquid products. Its smooth, glistening appearance might suggest its formation by a process of electrical deposition. On the other hand, it should be recalled that a similar solid film (suboxide of carbon) was formed in carbon monoxide[12] under action of a-rays where there was no electrical field, so that the action may be merely a surface condensation.

The variation in the average molecular weight of the liquid product appears to depend (Table I) on the length of time the earlier products remain in the discharge chamber subject to further ionization either in the gaseous or liquid state. Regulation of this factor by the two means already discussed appears to afford satisfactory control of the degree of condensation.

Some evidence of delayed condensation even in the gas phase has been discovered. The efficiency of condensation in long spiral traps at -50 to $-58°$ has been surprisingly low. To prove that it was really a chemical condensation taking place in the gas phase and not merely slow physical condensation in the trap or slow solution of low hydrocarbons in liquids already condensed, the following experiment was made. Four traps were placed in series at the same low temperature ($-50°$) with connecting tubes at ordinary temperature, spaced as shown below and in Fig. 2. The order of liquid volumes condensed was $(1) > (3) >> (2) > (4)$, showing that the longer

$$(1) \xrightarrow{\text{short}} (2) \overset{\text{long}}{\rule{8em}{0.4pt}} (3) \xrightarrow{\text{short}} (4)$$

time elapsing in passage of gas from 2 to **3** allowed further polymerization at ordinary temperature. This slow polymerization may be attributed to the "open bonds" already referred to, which may, of course, play a role also in delayed polymerization in liquid or solids, the slower there on account of the slower diffusion.

We are indebted to Mr. John L. Wilson, who worked with us as Research Assistant of the American Petroleum Institute.

Summary

Silent, corona and high frequency discharges all cause the condensation of ethane to liquid with the liberation of permanent gases. The average molecular weight of the liquid products has been regulated between 467

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on account of little head. Since the ozonizer represents the slowest rate of formation, the liquid was there subjected to a greater amount of secondary action than in the other types of discharge and hence higher molecular weights prevail.

[12] Lind and Bardwell, THIS JOURNAL, 47, 2683 (1925).

and 105 by controlling the time that the first products, either gaseous or liquid, are allowed to stay in the discharge tube—the more secondary action the higher the molecular weight owing to further condensation.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE ROCKEFELLER PHYSICAL AND BAKER CHEMICAL LABORATORIES OF CORNELL UNIVERSITY]

THE ABSORPTION SPECTRA OF HYDROQUINOLPHTHALEIN AND HYDROQUINOLSULFONEPHTHALEIN

BY C. V. SHAPIRO[1]

RECEIVED MARCH 24, 1928 PUBLISHED JUNE 5, 1928

The present investigation on the absorption spectra of hydroquinolphthalein and hydroquinolsulfonephthalein was undertaken not only to obtain possible corroborative evidence as to the existence of the meta-quinoid structure in these compounds and their salts, but also to contribute to our knowledge of the effect of hydroxyl substitution in the phthalein and triphenylmethane series generally.[2]

The preparation of hydroquinolsulfonephthalein has been described in a previous paper[3] and from its chemical behavior evidence has been advanced in favor of its possessing the meta-quinoid structure. A study of its absorption spectra, particularly in neutral and acid solution, reveals certain striking characteristics which differentiate it sharply from other sulfonephthaleins now being investigated in this Laboratory. Hence it may be provisionally assumed that to this extent the data support the view that the meta-quinoid configuration has a possible existence in the case of these hydroquinol derivatives. It is felt, however, that primary consideration must be given to the chemical evidence in settling this question, until more extensive data are available concerning the effect of hydroxyl substitution in the phthaleins and until more is known of the intrinsic nature of the several quinoid structures, ortho, meta and para. A comparison of the absorption spectra of hydroquinolphthalein and hydroquinolsulfonephthalein with those of their isomers, fluorescein[4a] and sulfonefluorescein,[4b] brings out a marked distinction. To what extent this difference is to be attributed to the different positions of the hydroxyl groups, or to the existence of different quinoid configurations, is still an unsettled question.

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[1] This article is based on a portion of a thesis presented to the Faculty of the Graduate School of Cornell University by the author, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Orndorff, Gibbs and co-workers, THIS JOURNAL, 47, 2767 (1925); 48, 1327, 1994 (1926); 49, 1541, 1545, 1588 (1927).

[3] Orndorff and Shapiro, THIS JOURNAL, 50, 1730 (1928).

[4] (a) Orndorff, Gibbs and Shapiro, (a) THIS JOURNAL, 50, 819 (1928); (b) Gibbs and Shapiro, *ibid.*, 50, 1755 (1928).

The absorption spectrum of hydroquinolphthalein has been studied by R. Meyer and his collaborators[5] in alkaline solution and by Howe[6] in neutral alcoholic solution. Moir,[7] working only in the visible region of the spectrum, has reported on its alkaline and sulfuric acid solutions.

Fig. 1 shows the absorption curves for hydroquinolphthalein and hydroquinolsulfonephthalein in absolute ethanol and for hydroquinolsulfonephthalein in distilled water. Curve A for hydroquinolphthalein exhibits four bands, of which the two at frequency numbers 3518 and 3626 are characteristic of the lactoid structure.[8] The absorption spectra of hydroquinolsulfonephthalein in ethanol and water, Curves B and C, run entirely parallel, with the bands for the alcohol solution displaced toward lower frequency numbers and exhibiting in general a lower intensity. The amount of the displacement is not uniform for the different bands, varying from 20 frequency units in one case up to 59. The significance of this similarity will be considered below in dealing with the acid solutions. Hydroquinolphthalein, admittedly lactoid, yields an absorption spectrum which bears a close relation to those observed for other lactoid phthaleins; on the other hand, hydroquinolsulfonephthalein, which is quinoid, does not resemble in absorption spectra either phenolsulfonephthalein or *o*-cresolsulfonephthalein, although both of these latter compounds have like spectra.[9] It appears reasonable, therefore, to attribute this difference in absorption spectra in part to a difference in internal structure, by denoting the hydroquinol derivative as meta-quinoid and the phenol and *o*-cresol compounds as para-quinoid.

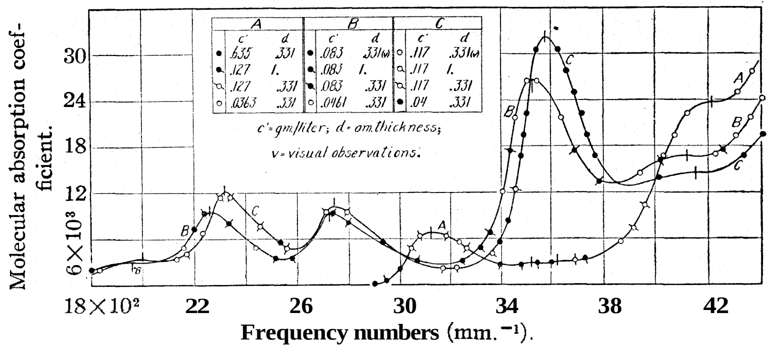

Fig. 1.—Neutral solutions. *A*, hydroquinolphthalein (alcoholic); *B*, hydroquinolsulfonephthalein (alcoholic); *C*, hydroquinolsulfonephthalein (aqueous).

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[5] R. Meyer and Marx, *Ber.*, 40, 3603 (1907); 41, 2446 (1908); R. Meyer and Fisher, *Ber.*, 44, 1944 (1911).

[6] Howe, Phys. *Rev.*, 8, 686 (1916).

[7] Moir, Trans. *Roy. Soc. S. Africa*, 7, 5 (1918).

[8] Gibbs and Shapiro, *Proc. Nat.* Acad. *Sci.*, 14, 251 (1928).

[9] Unpublished data.

The absorption spectra of the dibenzoates of hydroquinolphthalein and hydroquinolsulfonephthalein in ethanol solution are given in Fig. 2. The former dissolves to give a colorless solution and its spectrum, Curve A, shows four bands, of which the two at 3549 and 3676 are evidently due to the lactoid structure.[8] Curve B for the dibenzoate of hydroquinolsulfonephthalein is quite different in character, as it has bands in the visible and near ultraviolet regions, which are responsible for its yellow color, while in the further ultraviolet there are three bands which do not appear to be closely related to those of Curve A. The absence of the characteristic lactoid bands in the region of frequency number 3600 and the bright yellow color of the solution render it probable that this dibenzoate is quinoid in structure, in which case it must be derived directly from the inner salt form of hydroquinolsulfonephthalein.[3]

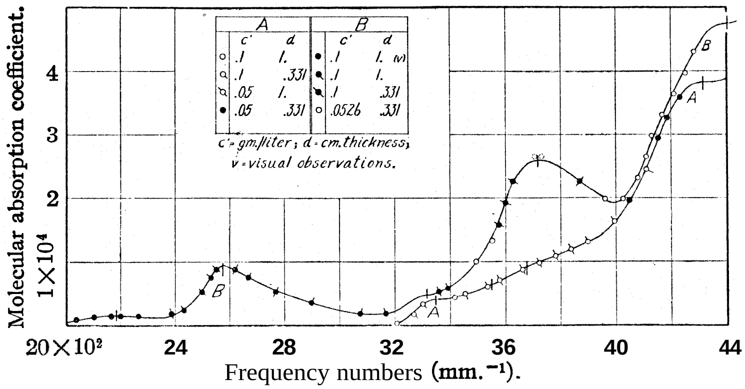

Fig. 2.—Neutral alcoholic solutions. *A*, hydroquinolphthalein dibenzoate; B, **hydroquinolsulfonephthalein** dibenzoate.

Hydroquinolphthalein and hydroquinolsulfonephthalein dissolve in concentrated sulfuric acid, yielding orange-yellow colored solutions. The absorption spectra are given in Fig. 3 and it will be noted that the curves are very nearly identical; the bands for hydroquinolphthalein, Curve A, are shifted slightly, though consistently, toward higher frequency numbers. Comparison of the curves of Fig. 3 with those for the neutral solutions of hydroquinolsulfonephthalein reveals a striking similarity, which is again evident in Fig. 4 for solutions of hydroquinolphthalein in alcoholic hydrogen chloride. This type of absorption, which is evidently due to salt formation, is entirely different from that which has been previously found for acid solutions of the other phthaleins and fluoresceins studied thus far. In the latter cases the absorption has been characterized by two prominent bands, one at either end of the spectrum. There have been slight variations: the far ultraviolet band in the fluoresceins[3] is double, while fuchsone, benzaurin and aurin[2] have shown a double band in the visible or near ultraviolet region. Since in all cases salt formation involves the quinoid structure, the exceptional behavior of hydroquinolphthalein and hydroquinolsulfonephthalein may again be attributed to the existence of the meta-quinoid state. That hydroquinolsulfonephthalein exists in the neutral condition as an inner salt is deduced from the general correspondence of the absorption curves for the neutral and sulfuric acid solutions, as well as for the acid solutions of hydroquinolphthalein. This is further corroborated by the non-formation of a hydrochloride when hydroquinolsulfonephthalein is exposed to dry hydrogen chloride[3] and by the fact that the addition of hydrogen chloride in ratios as high as 10,000 molecules to one of the sulfonephthalein produces no apparent effect on the absorption spectrum of the neutral solution. Phenol- and o-cresolsulfonephthalein in alcoholic solution have likewise been assigned inner salt structures on the basis of the similarity of their absorption spectra in neutral and acid solution.[9]

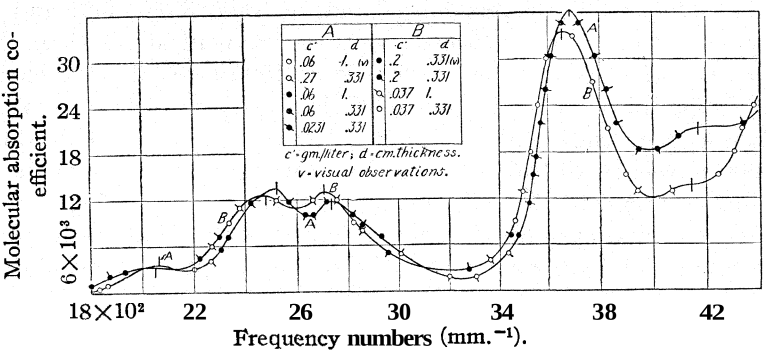

Fig. 3.—Concd. sulfuric acid solutions. A, hydroquinolphthalein; *B*, hydroquinolsulfonephthalein.

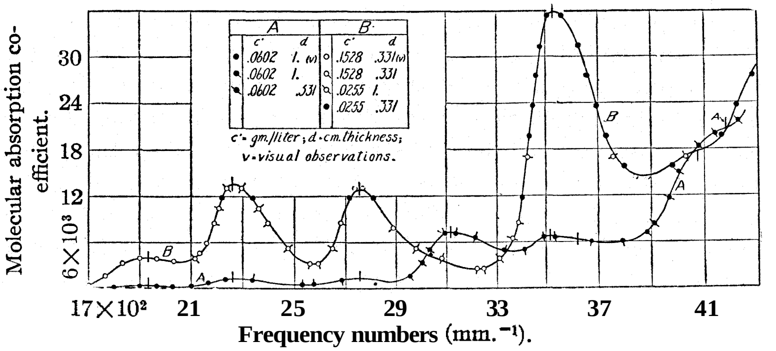

Fig. 4.—Hydroquinolphthalein in alcoholic HCl. A, 1 molecule:100 molecules HCl; B, 1 molecule:10,000 molecules HCl.

Fig. 4 shows the effect of adding various amounts of dry hydrogen chloride gas to an alcoholic solution of hydroquinolphthalein. Curve A for 1000 molecules of hydrogen chloride to one of the phthalein is a transition stage, as bands characteristic of both the neutral and acid condition are present. Thus the bands at 1933, 2259 and 2756 of Curve A occur in Curve B for 10,000 molecules of hydrogen chloride at 1933, 2260 and 2755, while the remaining bands at 3117, 3517, 3621 and 418% correspond to the four analogous bands in the neutral solution. That the presence of so large an excess of acid as 1000 molecules is ineffective in converting all of the hydroquinolphthalein into the hydrochloride may be taken as a measure of the strength of the lactoid bond. The addition of 10,000 molecules of hydrogen chloride brings out the whole of the acid spectrum as found in the sulfuric acid solution (Curve A, Fig. 3). For purposes of comparison, the frequency numbers of the bands in the various acid solutions of hydroquinolphthalein and hydroquinolsulfonephthalein are listed in Table I.

TABLE I

FREQUENCY NUMBERS OF BANDS IN NEUTRAL AND ACID SOLUTIONS

Substance	Solvent	Frequency Numbers of Bands				
Hydroquinolphthalein	**Alcoholic HCl**	**1933**	**2260**	**2755**	**3528**	**4075**
Hydroquinolphthalein	Concd. H_2SO_4	**2065**	**2523**	**2735**	**3685**	**4170**
Hydroquinolsulfonephthalein	**Absolute alcohol**	**1960**	**2259**	**2722**	**3523**	**4122**
Hydroquinolsulfonephthalein	**Distilled water**	**2000**	**2317**	**2742**	**3578**	**4153**
Hydroquinolsulfonephthalein	Concd. H_2SO_4	**2050**	**2481**	**2706**	**3656**	**4145**

Hydroquinolphthalein dissolves in aqueous solutions of potassium hydroxide with a blue color which fades out rapidly even in low ratios of alkali. In an alcoholic solution the color is very much fainter but, on the other hand, is much more stable. The low intensity is probably due to the slight dissociation of the dipotassium salt in the alcohol; in this respect hydroquinolphthalein is exceptional, as all of the phthaleins previously studied show the full color development in alcoholic as well as in aqueous alkaline solution. The absorption of an alcoholic solution containing 100 molecules of potassium hydroxide to one of the phthalein is shown in Fig. 5, Curve **A,** A', and is characterized by three bands. At lower ratios of alkali it was observed that bands due to both the neutral compound and its salt were present, the bands of the former becoming more prominent as the dilution was increased. This reversion effect has previously been noted with dilute, slightly alkaline solutions of phenolphthalein[2] and fluorescein[3] and is to be directly correlated with the weakly acid properties of these compounds. On dissolving hydroquinolphthalein in 33% aqueous potassium hydroxide, a colorless solution is at once obtained due to the formation of the tripotassium salt of the carbinol acid. The absorption spectrum of this solution is given by Curve B; its two bands are shifted toward the further ultraviolet relative to the corresponding bands of Curve A for the alcoholic alkaline solution. It is, therefore, probable that in the alcoholic solution the colored dipotassium salt is in equilibrium with the colorless tripotassium salt.

The effect of adding alkali to an alcoholic solution of hydroquinolsulfonephthalein leads to somewhat more complex phenomena, owing to the existence of the inner salt bond. The addition of the theoretical amount of potassium hydroxide, two molecules, is not sufficient to rupture this linkage completely and the color of the resulting solution is olive-green, due to the simultaneous presence of the orange-yellow neutral compound and of the blue alkali salt. It is a curious fact that dilution of such a solution does not result in reversion to the neutral color. This may be explained by the strong acid properties of free hydroquinolsulfonephthalein: its salts are not appreciably hydrolyzed in dilute solution.

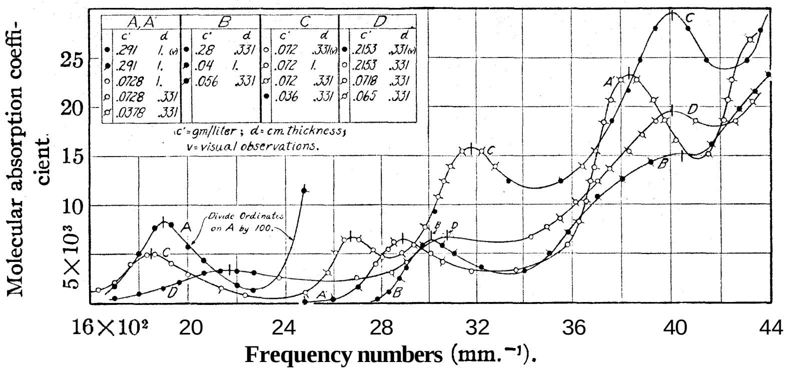

Fig. 5.—Alkaline solutions. Hydroquinolphthalein: A, 1 molecule: 100 molecules KOH (alcoholic); *B*, 33% ROH (aqueous). Hydroquinolsulfonephthalein; *C*, 1 molecule: 100 molecules KOH (alcoholic); D, 33% KOH (aqueous).

It is because of these strong acid properties that hydroquinolsulfonephthalein so readily forms an inner salt. Increasing the ratio of potassium hydroxide to four molecules yields a solution with a more bluish tint, as the concentration of the dipotassium salt is increased at the expense of the inner salt. At 100 molecules of alkali the color has become a pure blue-purple and the absorption spectrum of this solution is represented by Curve C, Fig. 5. There are four bands, as contrasted with the three for an analogous solution of hydroquinolphthalein, but the curves are generally similar in form. Dissolving hydroquinolsulfonephthalein in 33% aqueous potassium hydroxide results in a solution with a pale tan color, the absorption of which is given by Curve D. It is probable that the sulfonephthalein has been converted into the colorless tripotassium salt of the carbinol acid and that the slight color is due to a small amount of an oxidation product, for hydroquinolsulfonephthalein oxidizes with extreme ease in alkaline solution. That the solution contains primarily the tripotassium salt is confirmed by the close similarity in intensity and form of the ultraviolet portion of Curve D with Curve B for the tripotassium salt of hydroquinolphthalein.

The frequency numbers of the absorption bands for the various solutions studied are presented in Table II, with the exception of the acid solutions, the data for which have been listed in Table I.

TABLE II

FREQUENCY NUMBERS OF BANDS IN NEUTRAL AND ALKALINE SOLUTIONS

Solvent	Hydroquinolphthalein	Hydroquinolsulfonephthalein	Hydroquinolphthalein dibenzoate	Hydroquinolsulfonephthalein dibenzoate
		1960		
		2259		2185
Absolute	3121	2722	3347	2575
Ethanol	3518	3523	3549	3316
	3626	4122	3676	3715
	4213		4316	4410
Alcoholic	1900	1850		
KOH	2888	2670		
(100 m.)		3179		
	3833	4010		
33%		2170		
aqueous	3008	3076		
KOH	4048	4007		

The author is indebted to Professor R. C. Gibbs of the Physics Department for many helpful suggestions during the course of this investigation and to the Heckscher Research Foundation of Cornell University for the use of its spectrophotometric apparatus.

Summary

1. Evidence is submitted from a study of absorption spectra which provisionally confirms a conclusion previously arrived at from the chemical behavior of the compounds, that hydroquinolphthalein and hydroquinolsulfonephthalein can exist in the meta-quinoid state. It is also established that hydroquinolsulfonephthalein has an inner salt structure.
2. Data and curves are presented showing the absorption of these two compounds in neutral, acid and alkaline solutions.
3. **A** comparison of the absorption spectra of the dibenzoates of hydroquinolphthalein and hydroquinolsulfonephthalein shows that the latter is to be considered as a quinoid derivative.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE THERMAL DISSOCIATION OF ETHANE, PROPANE, NORMAL BUTANE AND ISOBUTANE. PRELIMINARY STUDY[1]

BY ROBERT N. PEASE[2]

RECEIVED MARCH 31, 1928 PUBLISHED JUNE 5, 1928

In view of the fundamental importance in petroleum chemistry of the thermal dissociation of hydrocarbons, it is surprising to find how few quantitative data on the subject have been published. Only methane and ethane, the lowest members of the series of aliphatic saturated hydrocarbons, have been studied at all thoroughly, and in these cases the published work is by no means exhaustive. This field is attractive in both its theoretical and practical aspects. It is to be hoped that catalytic methods may prove of value. Before these are applied, however, some information as to the uncatalyzed reactions is highly desirable. On this account we have made a preliminary study of the thermal dissociation of propane, normal butane and isobutane. A somewhat more thorough investigation on ethane is in progress. The results of the preliminary investigation are given in this report. The work is being continued.

Experimental Method

The flow method has been used. The gases were passed at measured rates through a heated tube of known volume and the products collected, analyzed and measured.

The only experimental difficulty concerns the gas analysis, and this is a serious one. It is an easy matter to determine the total unsaturated hydrocarbons by absorption in dilute bromine water, hydrogen by fractional combustion with copper oxide at 300–350°, and the total saturated hydrocarbons by combustion with copper oxide at 500–550°, as well as the average composition of the latter by absorption in caustic solution of the carbon dioxide formed on combustion. A more detailed analysis requires liquefaction and fractionation, which must be closely controlled if it is desired to distinguish isomers such as normal butane and isobutane. In this preliminary investigation, we have limited ourselves to a single separation at $-79°$, measuring and analyzing both the condensed and uncondensed fractions. At this temperature about $^1/_5$ of the hydrogen

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[1] This paper contains results obtained in an investigation on Catalytic Methods Applied to Petroleum Hydrocarbons listed as Project 7 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 cooperation of the Central Petroleum Committee of the National Research Council. The Director of Project No. 7 is Professor Hugh S. Taylor of Princeton University.

[2] Research Associate, American Petroleum Institute.

and probably $^1/_4$ to $^1/_2$ of the methane dissolves in the condensate. Analysis of the uncondensed portions proved that the saturated hydrocarbons therein must be chiefly methane, and when allowance was made for the original hydrocarbon uncondensed (the vapor pressure of propane at $-79°$ is 0.18 atm., and of butane is 0.015 atm,) the balance corresponded very closely to methane. This separation therefore sets a minimum to the amount of methane formed. A maximum is obtained by assuming that the only saturated hydrocarbons in the analyzed gases are the original and methane.

The gases which were used were obtained compressed in cylinders. Their behavior on condensation indicated a high degree of purity of all except the ethane. The analyses which follow have been calculated in terms of the chief constituent and that next higher or lower in the series according as the ratio of carbon dioxide to hydrocarbon was higher or lower than the ideal value. Ethane—C_2H_6, 83.5%; CH_4, 15.0%; N_2, 1.5%. Propane—C_3H_8, 97.5%; C_2H_6, 2.0%; N_2, 0.5%. *n*-Butane—C_4H_{10}, 97.5%; C_5H_{12}, 2.0%; N_2, 0.5%. *Iso*butane—C_4H_{10}, 97.5%; C_3H_8, 2.0%; N_2, 0.5%.

The arrangement of apparatus and the procedure were as follows. The gas passed from the cylinder to a calibrated resistance-tube flowmeter, equipped with a water overflow to keep the inlet pressure constant. The gas was then dried with calcium chloride and entered the heated reaction tube (of Pyrex) through a capillary tube. The outlet capillary was connected through a 3-way stopcock to a 500cc. gas receiver filled with mercury. When the gas was being collected, mercury was run out of the latter into a large leveling bulb through a capillary stopcock. By delicate regulation of this stopcock, it was possible to keep the flowmeter level exactly on the mark while collecting the whole of the off-gas.

The furnace consisted of a sheet iron core, 4 inches in diameter and 15 inches long, wound with heavy nichrome ribbon over asbestos paper. It was jacketed with magnesia pipe covering. The reaction tube occupied the middle 4 inches. The ends of the furnace were packed with loose magnesia and stopped with pieces of asbestos board. The middle section was found to be uniform in temperature to $\pm 2°$.

Temperatures were measured with a calibrated chromel-alumel thermocouple encased in a Pyrex tube which was ordinarily in contact with the center of the reaction tube.

In making a run, the furnace was brought to temperature and the gas flow started, ample time ($^1/_2$–1 hour) being allowed to attain a steady state. The exit tube was then connected with the gas receiver on the minute and the whole of the off-gas collected for exactly ten minutes. During this time the flow was kept constant as already indicated, and the temperature was closely controlled by hand regulation of the heating current. The off-gas was then divided into two fractions by passing through a trap held at $-79°$ into another reservoir. Five slow passages back and forth were carried out. Each fraction was then measured and analyzed.

The contact time was obtained by dividing the volume of the reaction tube by the mean of the volumes of entering and exit gas passing per second, this mean being corrected to the temperature of the tube.

Interpretation of Experimental Data

Our results give the composition and volume of gas introduced, the volume of each of the two fractions, and their composition in terms of total unsaturated hydrocarbons, hydrogen and total saturated hydrocarbons together with the average composition of the latter. The following preliminary conclusions concerning the reactions can be drawn.

There is always a volume increase on reaction, and this increase is very nearly equal to the volume of unsaturated hydrocarbons obtained. It is also true that the volume of saturated hydrocarbon plus hydrogen in the off-gas is equal to that of saturated hydrocarbon introduced. These facts suggest a primary dissociation into olefin and hydrogen, or into olefin and saturated hydrocarbon; thus (in the case of propane)

$$C_3H_8 = C_3H_6 + H_2 \text{ or}$$
$$C_3H_8 = C_2H_4 + CH_4$$

If this view is correct and there are no secondary reactions, the volume of original hydrocarbon dissociated, the volume of lower saturated hydrocarbon formed plus the hydrogen formed, and the volume of unsaturated hydrocarbon should all be the same. Since the composition of saturated hydrocarbon in the off-gas is only known as an average, this comparison cannot be made directly. We can, however, make some assumption as to the nature of the saturated hydrocarbon formed, and then compare the result with the above deduction. When this is done, it is found that if the equality of volumes is to hold, the hydrocarbon cannot be higher than methane in any case. Our analysis of the fraction uncondensed at $-79°$ gives a lower limit to the amount of methane, which accounts for a half to three-quarters of the total. The remainder remains indefinite, but for the present we prefer to calculate the whole as methane and we have reported it as such. Work now under way will give more definite results on this point.

In the following tables we give the contact time in seconds, the volume of hydrocarbon introduced in ten minutes (the time over which the off-gas was collected), the volume of original hydrocarbon recovered (calculated by difference, assuming the balance is methane) and the volumes of methane, hydrogen and total unsaturated hydrocarbons formed. In addition we give the percentages of dehydrogenation, "dernethanation," and of loss.

Results

In Table I are given the results of comparable experiments on the dissociation of ethane, propane, n-butane and *iso*butane at 650° and 1 atm. pressure at an average contact time of 11 seconds (reaction tube 15.2 cc. volume; volume of hydrocarbon in, 250 cc. in ten minutes).

It is evident from Table I that under these conditions the total amount of hydrocarbon dissociated increases with the number of atoms in the molecule, the butanes being most rapidly dissociated and ethane least rapidly. The amount of hydrogen obtained from ethane, propane and n-butane is of the same order, while the amount of methane increases, so that it is to increased amount of demethanation that the greater disso-

TABLE I

THERMAL DISSOCIATION OF C_2H_6, C_3H_8, n-C_4H_{10} AND *Iso*-C_4H_{10} AT 650°

Hydrocarbon	Contact time, secs.	Vol. H.C.[a] in cc.	Orig. H.C.	Off-gas in cc. C_nH_{2n}	Off-gas in cc. CH_4	Off-gas in cc. H_2	Loss	Percentage to CH_4	Percentage to H_2	Percentage to CH_4+H_2
C_2H_6	12	208	187	17	0	17	2	0	8	8
C_3H_8	11	249	172	53	41	22	6	16	9	25
n-C_4H_{10}	10	248	144	88	82	15	3	33	6	39
Iso-C_4H_{10}	11	248	138	73	57	40	5	23	16	39

[a] We include in the totals of hydrocarbons introduced the small amounts of foreign hydrocarbons, except in the case of ethane, when 38 cc. of methane was also present.

ciation of the higher normal hydrocarbons is due. *Iso*butane dissociates at the same rate as normal butane but gives a very different ratio of products. Thus, 40% of the isobutane dissociated is dehydrogenated as against 15% of the normal butane. It would seem, therefore, that the total rate of dissociation is a function of the size of the molecule only, while the nature of the products depends on the structure.

Further data on the dissociation of propane, normal butane and *iso*-butane at other rates are given in Table II.

TABLE II

INFLUENCE OF CHANGING CONTACT TIME ON THE DISSOCIATION OR C_3H_8, n-C_4H_{10} AND *Iso*-C_4H_{10} AT 650° AND 1 ATM.

Hydrocarbon	Contact time, secs.	Vol. H.C. in cc.	Orig. H.C.	Off-gas in cc. C_nH_{2n}	Off-gas in cc. CH_4	Off-gas in cc. H_2	Loss	Percentage to CH_4	Percentage to H_2	Percentage to CH_4+H_2
C_3H_8	6	254	208	37	31	18	−1	12	7	19
	11	249	172	53	41	22	6	16	9	25
	21	272	177	69	64	29	1	24	11	36
n-C_4H_{10}	8	226	164	67	54	10	−1	24	4	28
	10	248	144	88	82	15	3	33	6	39
	21	242	140	105	86	17	0	36	7	43
Iso-C_4H_{10}	8	206	144	51	37	29	−2	18	14	32
	11	248	138	73	57	40	5	23	16	39
	22	239	123	96	77	45	−2	32	19	51

Table II shows that the ratio of demethanation to dehydrogenation does not vary greatly with the total amount of dissociation. It also would appear that the rate diminishes rather rapidly with the concentration of hydrocarbon, but under the conditions of the experiment, and in view of the uncertainty as to the precise nature of the products, it is not possible to state definitely what the reaction order is.

In order to determine whether the hydrogen which is formed enters into secondary reaction with the hydrocarbons, two experiments were carried out with normal butane, in one of which the butane was diluted with one-half its volume of hydrogen and in the other with one-half its volume of nitrogen. The latter experiment was to serve as a check on the effect of dilution by hydrogen as opposed to chemical reaction. The results are given in Table III.

TABLE III

EFFECT OF DILUTION OF NORMAL BUTANE WITH HYDROGEN AND WITH NITROGEN AT 650° AND 1 ATM.

2 Vols. C_4H_{10} plus 1 vol. of	Contact time, secs.	H.C. in, cc.	Off-gas in cc. Orig. H.C.				Percentage to Loss			
			Orig. H.C.	C_nH_{2n}	CH_4	H_2	Loss	CH_4	H_2	CH_4+H_2
Hydrogen	7	248	161	71	61	17[a]	3	25	7	32
Nitrogen	7	248	162	72	63	12	3	25	5	30

[a] Exclusive of 125 cc. of hydrogen introduced.

Since the results of the two experiments correspond within experimental error, we conclude that hydrogen acts simply as a diluent, and that in the other experiments there is no appreciable reaction of the hydrogen formed either with the saturated hydrocarbons or with the olefins.

Comparison of these results with that obtained with *n*-butane alone at 1 atm. pressure and 8 seconds' contact (instead of 7 seconds) shows that the percentage conversion is nearly the same. This is what would be expected if the reactions are unimolecular. The fractional conversion should then be independent of dilution.

Finally, we have carried out comparable experiments on propane, n-butane and *iso*butane at 625 and 650" to get an idea of the temperature influence. The results of these are given in Table IV.

TABLE IV

TEMPERATURE INFLUENCE ON THE DISSOCIATION OF C_3H_8, *n*-C_4H_{10} AND *Iso*-C_4H_{10} EXPERIMENTS AT 625 AND 650°

Hydro-carbon	Temp., °C.	Contact Time, secs.	H.C. in cc.	Off-gas in cc.				Percentage to			
				Orig. H.C.	C_nH_{2n}	CH_4	H_2	Loss	CH_4	H_2	CH_4+H_2
C_3H_8	625	22	272	204	43	39	21	3	14	8	22
	650	21	272	177	69	64	29	1	24	11	35
n-C_4H_{10}	625	24	242	165	69	63	11	1	26	5	31
	650	21	242	140	105	86	17	0	36	7	43
Iso-C_4H_{10}	625	24	239	170	59	39	30	0	16	13	29
	650	22	239	123	96	77	45	2	32	19	51

We find that the ratios of the percentage dissociation at the two temperatures are of the order of 1.5 to 2 per 25° under these conditions. This would correspond to an activation energy of 25,000–50,000 cal. per mole. Since dissociation has taken place to a considerable extent, these figures are lower than the true values for these quantities.

Discussion

The general results of these experiments can be satisfactorily accounted for qualitatively. Modern theories of reaction rate indicate that a molecule which is about to react contains energy in excess of the average of all molecules. More particularly, the excess is associated with one or more degrees of freedom which, in the cases under consideration, doubtless represent the oscillation of atoms about their positions of equilibrium.

Heat capacity data prove that the total energy available for concentration on some particular degree of freedom increases with the number of atoms in the molecule (and also with the temperature, of course). The frequency with which a molecule finds itself active will therefore be greater the more complex the molecule, so that if the energy required for activation is of the same order for molecules of two substances of differing complexity, the frequency with which the more complex molecules react will be the greater.

If the molecule can undergo more than one type of reaction, the relative ratio of the different types will depend on the relative magnitude of the energy quantities required for activation. There is evidence based on thermal data that the energy required for the complete destruction of a carbon–carbon linkage is about 72,000 cal. per mole and for a carbon–hydrogen linkage about 92,000 cal. per mole. If we assume that in order to produce methane a carbon–carbon linkage must first be broken, while to produce hydrogen a carbon–hydrogen linkage must first be broken, we have an explanation of the fact that when both these reactions can take place, demethanation occurs to the greater extent (because it is associated with a lesser energy of activation). Some variation from strict constancy of the ratio of demethanation to dehydrogenation is to be expected due to minor variations in the energies of C–C and C–H linkages in different hydrocarbons. Thus, it is well known that a tertiary hydrogen atom, such as exists in isobutane, is in general more reactive than hydrogen formed in other ways. We thus may expect, and find, a greater proportion of dehydrogenation in this case.

Recent experiments having shown that the dissociation of ethane and of propane is unaffected by an increase in glass surface, we conclude that all these reactions are homogeneous gas reactions. The order is probably the first, as already pointed out.

The above considerations appear to give a rational explanation of the results which have been obtained and we propose to adopt them as a working hypothesis in the succeeding work.

Summary

The thermal dissociations of ethane, propane, normal butane and *iso*butane have been studied at 625 and 650°, and 1 atm. We find that the total rate of dissociation increases with the complexity of the molecule. The two principal reactions are dehydrogenation and demethanation. The ratios of hydrogen to methane decrease in the series ethane, propane, n-butane. Isobutane decomposes at about the same rate as n-butane but gives relatively much more hydrogen. The hydrogen formed undergoes no appreciable secondary reaction. The reactions seem to be somewhat more rapid than normal in the first few seconds but dilution experiments

indicate a first order reaction. The temperature coefficients are as a minimum 1.5–2 per 25°, giving a minimum activation energy of 25,000–50,000 cal.

An explanation of the relative rates of the reactions is given in terms of activation energies as a function of the size of the molecule and the nature of the linkages to be broken.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING LABORATORY OF SYRACUSE UNIVERSITY]

THE MELTING POINT OF META-DINITROBENZENE

BY FRANCES McCAMISH AND ALBERT SALATHE

RECEIVED APRIL 2, 1928 PUBLISHED JUNE 5, 1928

Answering a call issued by J. E. Zanetti,[1] we have carefully determined the melting point of *m*-dinitrobenzene; ninety degrees is commonly given in the textbooks. We used Washburn's[2] method, employing an unsilvered half pint thermos bottle furnished by the Icy Hot Company. The bottle, padded with asbestos except for a small opening through which the thermometer was read, was heated carefully on the sand-bath to about 100 degrees and then allowed to cool during half an hour or forty-five minutes. The solidification temperature was constant over a period of from ten to fifteen minutes. With recrystallized material from the DuPont Company, the following (corrected) results were obtained.

I	89.583	IV	89.553
II	89.593	V	89.563
III	89.563	Mean	89.57

The determinations represent fresh samples in each case, for the melting was found to cause discoloration and decomposition which lowered the solidification point several tenths of a degree. Material that had been melted was recrystallized from alcohol. The solidification point was no higher than that of the DuPont material which was labeled "89.8–89.95 degrees." We made three capillary tube melting point determinations, using hot water as the bath, and found 89.85 degrees for the average. An Anschuetz thermometer, calibrated by the Bureau of Standards, was used throughout.

The work was done at Sweet Briar College in the spring of 1924. The International Critical Tables give 89.7 as the melting point.

SYRACUSE, NEW YORK

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[1] Zanetti, *Ind. Eng. Chem.*, 16, 88 (1924).

[2] Washburn, *ibid.*, 16,275 (1924).

[CONTRIBUTION NO. 26 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

THE CATALYTIC PREPARATION OF METHYLAMINE FROM METHYL ALCOHOL AND AMMONIA[1]

BY TENNEY L. DAVIS AND ROBERT C. ELDERFIELD

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Except for the methods which use prussic acid and acetamide as raw materials, the most useful processes for the preparation of methylamine are those which start with some derivative of methyl alcohol or with formaldehyde which is itself prepared by the oxidation of methyl alcohol. We have therefore sought for a method by which methylamine, preferably free from secondary and tertiary amine, may be procured directly from methyl alcohol without intermediate steps.

Sabatier and Mailhe[2] have found that various alcohols react with ammonia when the vapors are passed over thorium oxide at 350–370°; water is eliminated and the primary amine is formed. They have found also that primary amines react with alcohols in the same way to yield secondary amines and have reported the preparation of a number of primary and secondary amines and of some secondary amines containing dissimilar groups. They did not work with methyl alcohol; their materials in every case were such that the products could be separated by ordinary distillation and they did not report the yields.

We find that the reaction between methyl alcohol and ammonia in presence of hot thorium oxide results in the conversion of a portion of the materials into methylamine and have studied the reaction under various conditions by collecting the products in hydrochloric acid and analyzing the mixed chlorides. The best results are secured at 325–330° and the yield drops off very sharply both above and below this temperature. At higher temperatures, especially above 380°, the catalyst becomes coated with carbonaceous material and the methyl alcohol is decomposed with the formation of carbon monoxide and hydrogen along with methane and some formaldehyde. Since the use of this reaction for the preparation of methylamine involves the separation of that substance from unchanged ammonia,[3] we have made no effort to increase the

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[1] The present work was undertaken on behalf of the Ordnance Department, and this report if it is published with the permission of the Chief of Ordnance.

[2] Sabatier and Mailhe, *Compt. rend.*, 148, 898 (1909).

[3] The method described by Valton, *J. Chem. Soc.*, **127**, 40 (1925), has special advantages for the explosives maker. The mixture of methylamine and ammonia is absorbed in an alcohol solution of 2,4-dinitrochlorobenzene. On standing overnight at ordinary temperature the methylamine reacts and the next morning 2,4-dinitromethylaniline is crystallized out practically pure and in practically quantitative amount. The ammonia reacts only on longer standing. Tetryl or 2,4,6-trinitrophenylmethylnitramine may be obtained from 2,4-dinitromethylaniline by simple nitration.

yield by the use of an excess of ammonia. The separation of methyl alcohol from methylamine, on the other hand, is easy and we have made experiments to determine what excess of methyl alcohol must be used to secure the largest conversion of methyl alcohol into methylamine. The results indicate that 80–83% of a mole of ammonia per mole of methyl alcohol will bring about the maximum conversion, namely, that of about *32.5%* of the methyl alcohol into methylamine. The product, although formed in the presence of methyl alcohol, contains no secondary or tertiary amine.

Discussion of Experiments

The methyl alcohol which was used was the ordinary commercial material and the ammonia was obtained from a cylinder of the liquefied gas.

The catalyst was prepared according to the method of Kramer and Reid,[4] and consisted of fragments of pumice, between 6 and 12 mesh, impregnated with **3** times its own weight of thorium oxide (from the nitrate). It had been heated in a current of air at 270" for the decomposition of the nitrate and finally at 400° until the issuing gases no longer reddened litmus paper. After the catalyst had become coated with carbonaceous material by use at 380° and above, it was conveniently regenerated by heating at 380°, first with steam, then with nitrogen peroxide, and finally with steam again.

The reaction chamber consisted of an electrically heated quartz tube of **27** mm. internal diameter and about 125 cm. long. The catalyst occupied a length of about 1 meter. The temperature was determined by means of a thermocouple inside the tube. The ammonia was admitted from a cylinder of the liquefied gas and its amount was determined by a calibrated flowmeter of the standard orifice type to which was connected an inclined U-tube to permit of more accurate control. The alcohol was admitted from a vaporizer which consisted of a distilling flask heated in an oil-bath and equipped with a dropping funnel from which the alcohol dropped into the flask, where it was immediately vaporized. The pressure in the distilling flask and in the upper part of the dropping funnel was equalized by a connecting glass tube. The escaping gases from the reaction were absorbed by 25% hydrochloric acid which trickled down an absorption tower consisting of a glass condenser jacket filled with short pieces of glass tubing. At the end of each run a considerable amount of condensed water and methyl alcohol was found entrapped in the cold exit end of the quartz tube. This was added to the acid liquor from the absorption tower, the whole was evaporated to dryness and the residue, after baking at 105°, was analyzed for chlorine by titration with silver nitrate. Since tests showed that the product contained no secondary or tertiary amine, it was possible to calculate the amount of methylamine hydrochloride which was mixed with the ammonium chloride.

A series of runs was carried out for the purpose of determining the best temperature for the reaction and the most favorable relative concentration of the reacting gases. Each run required two hours for the passage of the materials through the catalyst chamber. The yields, in the table below, are the percentages of ammonia which was converted into methylamine.

If these data are plotted, the three curves have a maximum at about the

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[4] Kramer and Reid, THIS JOURNAL, 43, 883 (1921).

TABLE I

YIELDS OF METHYLAMINE

Gram molecules of NH_3	0.5	0.75	1.0
Gram molecules of CH_3OH	1.0	1.0	1.0
Temp., °C.	Yield, %	Yield, %	Yield, %
275	31.5	26.1	14.7
280	...	28.4	...
285	...		23.1
290	33.8	29.5	16.7
300	...	24.5	22.0
305	38.4		
310	...	29.6	
315	39.9	...	
325	41.6; 41.7	37.5	...
330	41.5	42.4	25.5; 24.1
335	33.8		25.9
350	29.0; 30.6	35.5	23.0
360	33.8; 34.6	28.4	21.8
370	28.0	...	
375		19.6	...
385		...	16.1
400	21.2	9.1; 8.0	...
500	19.5	4.5	10.5

same point, namely, at 325–330°, and all three drop away rapidly on both sides of the maximum. We infer that 325–330° is the best temperature for the reaction. When the results at 330° are recalculated in terms of the percentage of methyl alcohol converted to methylamine, and are compared with the percentage of the theoretically required ammonia which was used, we have the following.

Theoretical ammonia, %	50.0	75.0	100.0
Methyl alcohol converted, %	20.75	31.8	25.5; 24.1

The curve representing these data has a maximum at a point which corresponds to about 80–83% of the theoretical ammonia and to about 32.5% of the methyl alcohol converted into methylamine.

In the experiments at higher temperatures it was noticed that an offensive odor, resembling that of decayed cabbage, came from the apparatus—the higher the temperature the stronger the odor. An examination of the chlorides for the amines, putrescine and cadaverine, was without result. An analysis of the gaseous products gave no clue to the nature of the odor but showed that the methyl alcohol had been broken down to form the primary and secondary products which would be expected in accordance with the earlier findings of other investigators. In the run at 475° in which 0.75 mole of ammonia was used, the gases were scrubbed thoroughly with hydrochloric acid, collected and analyzed. The results are shown in Column I.

	I—%	II—%
Carbon dioxide	4.40	6.40
Unsaturated hydrocarbons	1.14	1.30
Oxygen	1.83	1.41
Hydrogen	55.75	53.91
Garbonmonoxide	21.20	20.60
Methane	6.80	9.33
Nitrogen (by difference)	8.88	7.05
Nitrogen with oxygen from air leakage	7.32	5.64
Net nitrogen	1.56	1.41

In another experiment methyl alcohol vapor without ammonia was passed through the catalyst chamber at 475°, the gases were bubbled through water and the water was found to give a strong test with the fuchsine aldehyde reagent—indicating formaldehyde. The composition of the gases is shown in Col. II above. Since ammonia is appreciably decomposed into its elements at 475°, the nitrogen of the first experiment may be accounted for, and that of the second is probably to be explained by supposing that some ammonia was left in the catalyst chamber from the earlier runs. The presence of carbon monoxide and hydrogen is in agreement with the observation of Ghosh and Baksi,[5] who passed methyl alcohol vapor over a mixture of copper oxide with thorium oxide at 215° and obtained a gas which consisted of carbon dioxide 2.6%, carbon monoxide 13.2%, methane 5.2% and hydrogen 78.5%. Sabatier and Senderens[6] had previously produced methane, and Orlow[7] had produced ethylene, from the hydrogenation of carbon monoxide.

The reaction between methyl alcohol and ammonia which produces water and methylamine takes place, theoretically, without change of volume, and we have not studied the effect of pressure upon it. Since the most favorable temperature, 325–330°, is below the critical temperature of water, 365°, it is possible that an increase of pressure by causing a condensation of part of the water would result in an increased yield.

Summary

Methylamine is formed when methyl alcohol and ammonia are passed over a hot thorium oxide catalyst. The best temperature appears to be 325–330° and the best relative concentration about 0.80–0.83 mole of ammonia per mole of methyl alcohol. Under the best conditions nearly one-third of the methyl alcohol is converted into methylamine.

CAMBRIDGE, MASSACHUSETTS

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[5] Ghosh and Baksi, *Quart. J. Ind. Chem. Soc.*, [111]4,415 (1926).

[6] Sabatier and Senderens, *Ann. chim. phys.*, [8] 4, 418 (1905).

[7] Orlow, *Chem. Zent.*, 80, I, 735 (1909).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

A^2-CYCLOPENTENYLETHYL ALKYL ACETIC ACIDS AND THEIR BACTERICIDAL ACTION TOWARD B. LEPRAE. XII.[1]

BY J. A. ARVIN AND ROGER ADAMS[2]

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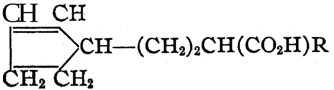
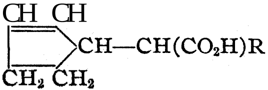
The fact that a Δ^2-cyclopentenyl group is present in chaulmoogric and hydnocarpic acids warrants a more extended investigation of synthetic acids containing this grouping than is described in an earlier paper. A complete series of Δ^2-cyclopentenylethyl alkyl acetic acids (I), where "R" varies from n-hexyl to *n*-lauryl, was prepared. This series was selected partly because of the comparative ease of preparation and partly because of the fact that it would probably be a more effective series than the A^2-cyclopentenyl alkyl acetic acids, judging from the greater effectiveness of cyclohexylethyl alkyl acetic acids over the cyclohexyl alkyl acetic acids.

A few members of the A^2-cyclopentenyl alkyl acetic series (II) where the "R" group is decyl, undecyl and lauryl were also made, since in the earlier investigation not a sufficient number of members of the series were prepared in order to show where the maximum action might be found.



I



II

In Tables I and II are given the bacteriological results on these compounds.

The most effective substances in Table I are those containing 16 to 19 carbon atoms in the molecule, as found for other acids previously described, and the degree of bactericidal action appears to be approximately the same as of those substances of essentially the same molecular weight found in other series.

TABLE I

Δ^2-CYCLOPENTENYLETHYL ALKYL ACETIC ACIDS, $C_5H_7(CH_2)_2CH(CO_2H)R$

	Dilutions of Sodium Salts in Thousands											
R =	25	36	50	62	74	85	100	125	147	165	192	230
C_6H_{13}	−	−	±	±	±	−	+	+	+	+	+	+
C_7H_{15}	−	−	−	−	−	−	±	−	−	−	*	+
C_8H_{17}	−	−	−	−	−	−	−	−	±	−	±	±
C_9H_{19}	−	−	−	−	−	−	−	−	−	+	−	+
$C_{10}H_{21}$	−	−	−	−	−	−	−	−	−	−	−	+
$C_{11}H_{23}$	−	−	−	−	−	±	±	±	+	+	+	+
$C_{12}H_{25}$	−	−	−	−	+	+	+	+	+	+	+	+

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[1] Paper XI in this series, Yohe and Adams, THIS JOURNAL, **50,** 1503 (1928).

[2] This communication is an abstract of a portion of a thesis submitted by J. A. Arvin in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

TABLE II

Δ^2-CYCLOPENTENYL ALKYL ACETIC ACIDS, $C_5H_7CH(CO_2H)R$

Dilutions of Sodium in Thousands

R =	10	20	30	40	50	60	70	80	90	100	111	125	133	143	153	167	176	185	200
n-$C_{10}H_{21}$	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	±	+	+
n-$C_{11}H_{23}$	−	−	−	−	−	−	−	−	−	−	−	−	+	+	+	+	+	+	+
n-$C_{12}H_{25}$	−	−	−	−	−	−	−	−	−	±	−	±	±	+	+	+	+	+	+
X =	Δ^2-CYCLOPENTENYL ALKYL ACETIC ACIDS, $C_5H_7(CH_2)_xCO_2H$																		
3	±	±	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
5	−	±	±	±	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

In Table III the maximum bactericidal action obtained with the most effective isomers in series analogous to those prepared in this investigation is given.

TABLE III

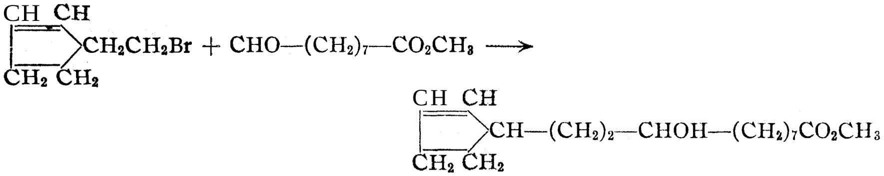
COMPARISON OF BACTERICIDAL EFFECT OF VARIOUS ANALOGS

	General Formula	R =	Max. effective dilution in thousands	Empirical formula
1.	$C_5H_7(CH_2)_2CH(CO_2H)R$ (cyclopentenyl)	n-C_7H_{15}	85	$C_{16}H_{28}O_2$
		n-C_8H_{17}	125	$C_{17}H_{30}O_2$
		n-C_9H_{19}	147	$C_{18}H_{32}O_2$
		n-$C_{10}H_{21}$	192	$C_{19}H_{34}O_2$
2.	$C_5H_7CH(CO_2H)R$ (cyclopentenyl)	n-C_9H_{19}	150	$C_{16}H_{28}O_2$
		n-$C_{10}H_{21}$	170	$C_{17}H_{30}O_2$
		n-$C_{11}H_{23}$	120	$C_{18}H_{32}O_2$
3.	$C_5H_9(CH_2)_2CH(CO_2H)R$ (cyclopentyl)	n-C_7H_{15}	160	$C_{16}H_{30}O_2$
		n-C_8H_{17}	170	$C_{17}H_{32}O_2$
4.	$C_5H_9CH(CO_2H)R$ (cyclopentyl)	n-C_9H_{19}	111	$C_{16}H_{30}O_2$
		n-$C_{10}H_{21}$	143	$C_{17}H_{32}O_2$
		n-$C_{11}H_{23}$	153	$C_{18}H_{34}O_2$
5.	$C_6H_{11}(CH_2)_2CH(CO_2H)R$ (cyclohexyl)	n-C_6H_{13}	160	$C_{16}H_{30}O_2$
		n-C_7H_{15}	220	$C_{17}H_{32}O_2$
		n-C_8H_{17}	320	$C_{18}H_{34}O_2$
6.	$C_6H_{11}CH(CO_2H)R$ (cyclohexyl)	n-C_8H_{17}	111	$C_{16}H_{30}O_2$
		n-C_9H_{19}	176	$C_{17}H_{32}O_2$
		n-$C_{10}H_{21}$	176	$C_{18}H_{34}O_2$
		n-$C_{11}H_{23}$	153	$C_{19}H_{36}O_2$

The differences between the bactericidal effects of compounds containing approximately the same number of carbon atoms is not significant enough to be worthy of discussion. It is of interest to note that by comparing series 1 and 2 with series 3 and 4 the olefin linkage has not produced any specific effect.

The chief raw material used for the preparation of these compounds was cyclopentenyl chloride, which has been described in previous articles. The cyclopentenylethyl bromide was prepared by the reduction of ethyl cyclopentenyl acetate, prepared in turn by the esterification of the acid produced by the malonic ester synthesis from cyclopentenyl chloride.

In earlier work an attempt was made by C. R. Noller to synthesize *d,l*-hydnocarpic acid by the condensation of A^2-cyclopentenylethyl magnesium bromide with methyl-8-aldehydo-octanoate and then elimination of the hydroxyl group. Before the work was entirely completed, the synthesis of *d,l*-chaulmoogric acid by Perkins through a different procedure led to the abandonment of the former research. Preparation of methyl-8-hydroxy-*d,l*-hydnocarpate and the corresponding acid had already been completed, so that the experimental results of Noller are described in this paper.



The bacteriological work was carried out by W. M. Stanley.

Experimental

A^2-Cyclopentenyl Ethanol.—This was prepared as described by Noller and Adams.[3]

Δ^2-Cyclopentenyl Ethyl Bromide.—A solution of **62.5** g. of cyclopentenyl ethanol in **150** cc. of dry toluene was cooled to $-5°$ and a solution of **50** g. of redistilled phosphorus tribromide in **100** cc. of toluene was added slowly with shaking at such a rate that the temperature did not rise above 0°. After the addition of the tribromide, the mixture was allowed to warm to room temperature, stand for one-half hour and was then heated on a steam-cone for one hour. The mixture was cooled, decomposed by pouring it into cold water, separated and the upper layer washed with a 5% solution of sodium hydroxide and then with water. The bromide thus obtained, after careful fractionation, boils at **71–72'** at **16 mm.** About **158** g. of bromide was obtained from **190** g. of alcohol; n_D^{20}, **1.4995;** d_4^{20}, **1.2869.**

Anal. Calcd. for $C_7H_{11}Br$: Br, **45.71.** Found: **47.48.**

Δ^2-Cyclopentenyl Butanol.—Δ^2-Cyclopentenyl ethyl magnesium bromide was condensed with ethylene oxide according to the procedure described by Hiers and Adams.[4] The average yield of the butanol was **38%;** b. p. 118–123° at **24** mm.; n_D^{20}, **1.4723;** d_4^{20}, **0.9317.** Calcd. for $C_9H_{16}O$: C, **77.09,** H, **11.52.** Found: C, **76.91;** El, **11.62.**

As a by-product a substance boiling from **98–103°** at **24** mm. was obtained, the structure of which was not determined.

A^2-Cyclopentenyl **Butyl Bromide.—A^2-Cyclopentenyl**butanol was converted to the bromide in a manner similar to the preparation of cyclopentenylethyl bromide from the correspondimg alcohol. The product formed in **47%** yields; b. p. **82–86'** at **5** mm.; n_D^{20}, **1.4942;** d_4^{20}, **1.2229.**

Anal. Subs., **0.3370; 13 98** cc. of **0.1193** *N* $AgNO_3$. Calcd. for $C_9H_{15}Br$: Br, **39.35.** Found: Br, **39.56.**

Diethyl A^2-Cyclopentenyl **Alkyl Malonates.—Diethyl** Δ^2-**cyclopentenylethyl** and diethyl **Δ^2-cyclopentenylbutyl malonates** were prepared by the condensation of the corresponding bromides and **malonic** ester in the usual way; yields were about 66–69%.

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[3] Noller with Adams, **This** JOURNAL, 48, **2444** (1926).

[4] **Hiers with** Adams, ***ibid.***, 48, **2385 (1926).**

Δ^2-Cyclopentenylalkyl Malonic Acids.—The malonic acids of this series were prepared according to the procedure described by Adams, Stanley and Stearns.[5] They were purified by recrystallization from benzene and were obtained in essentially quantitative yields.

Δ^2-Cyclopentenylethyl Acetic **Acids** and **Δ^2-Cyclopentenylbutyl** Acetic Acids.—These were prepared from the corresponding malonic acids by heating for a few hours at 150–155°.

Diethyl **Δ^2-Cyclopentenyl** and Diethyl **Δ^2-Cyclopentenylethyl Alkyl Malonates.**—

TABLE IV

DIETHYL Δ^2-CYCLOPENTENYLETHYL ALKYL MALONATES, $C_5H_7(CH_2)_2C(CO_2C_2H_5)_2R$

R =	B. p., °C.	n_D^{20}	d_4^{20}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
n-C_6H_{13}	152–155 (2 mm.)	1.4598	0.9742	70.94	10.13	70.90	10.15
n-C_7H_{15}	159–162 (1.4 mm.)	1.4602	.9649	71.53	10.30	71.76	10.33
n-C_8H_{17}	178–181 (2 mm.)	1.4605	.9624	72.07	10.46	71.73	10.41
n-C_9H_{19}	176–180 (1.5 mm.)	1.4609	.9567	72.57	10.60	72.47	10.62
n-$C_{10}H_{21}$	183–187 (2.1 mm.)	1.4613	.9531	73.04	10.73	72.94	10.95
n-$C_{11}H_{23}$	190–194 (2.1 mm.)	1.4616	.9486	73.47	10.86	73.25	10.80
n-$C_{12}H_{25}$	197–201 (2.2 mm.)	1.4618	.9460	73.87	10.98	73.49	11.03

DIETHYL Δ^2-CYCLOPENTENYL ALKYL MALONATES, $C_5H_7C(CO_2C_2H_5)_2R$

R =							
n-$C_{10}H_{21}$	170–172 (1.5 mm.)	1.4616	.9642	72.07	10.46	72.20	10.46
n-$C_{11}H_{23}$	176–180 (1 mm.)	1.4622	.9598	72.57	10.60	72.24	10.52
n-$C_{12}H_{25}$	193–196 (2 mm.)	1.4627	.9559	73.04	10.73	72.66	10.51

DIETHYL-ω-Δ^2-CYCLOPENTENYLALKYL MALONATES, $C_5H_7(CH_2)_xCH(CO_2C_2H_5)_2$

X =							
4	152–155 (3 mm.)	1.4598	1.0077	68.04	9.29	67.71	9.57

TABLE V

Δ^2-CYCLOPENTENYLETHYL ALKYL ACETIC ACIDS, $C_5H_7(CH_2)_2CH(CO_2H)R$

R =	M. p., °C.	B. p., °C.	n^{20}	d_4^{20}	Calcd., % C	Calcd., % H	Found, % C	Found, % H
n-C_6H_{13}	.....	160–163 (2.3 mm.)	1.4697	0.9426	75.57	10.99	75.43	11.17
n-C_7H_{15}	.....	166–168 (2.2 mm.)	1.4698	.9358	76.12	11.19	76.37	11.14
n-C_8H_{17}	.....	174–176 (1.8 mm.)	1.4700	.9315	76.62	11.37	76 62	11.30
n-C_9H_{19}	.....	183–185 (2 mm.)	1.4701	.9269	77.06	11.51	76.88	11.56
n-$C_{10}H_{21}$	.....	186–188 (1.5 mm.)	1.4702	.9227	77.47	11.65	77.33	11.73
n-$C_{11}H_{23}$	.....	190–193 (1.3 mm.)	1.4703	.9196	77.84	11.77	77.68	11.76
n-$C_{12}H_{25}$	30–31 5	199–203 (1.5 mm.)			78.18	11.89	77.97	11.82

Δ^2-CYCLOPENTENYL ALKYL ACETIC ACIDS, $C_5H_7CH(CO_2H)R$

R =								
n-$C_{10}H_{21}$	.....	183–186 (1.5 mm.)	1.4692	.9319	76.62	11.37	76.54	11 22
n-$C_{11}H_{23}$	36–38	188–190 (1.5 mm.)	....	...	77.06	11.51	76.72	11.39
n-$C_{12}H_{25}$	38–39	202–204 (2 mm.)	....	...	77.47	11.65	77.07	11.83

w-Δ^2-CYCLOPENTENYLALKYL ACETIC ACIDS, $C_5H_7(CH_2)_xCO_2H$

X =								
3		125–126 (4 mm.)	1.4718	,9904	70.14	9.16	70.16	9.52
5		149–154 (5 mm.)	1.4740	.9862	72.47	9.96	72.80	10.14

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[5] Adams, Stanley and Stearns, THIS JOURNAL, 50, 1475 (1928).

The diethyl Δ^2-cyclopentenyl alkyl malonates were prepared from diethyl Δ^2-cyclopentenyl malonate and the proper alkyl bromide by the procedure described by Adams, Stanley and Stearns.[5] The yields were 58–60%.

In a similar manner the Δ^2-cyclopentenylethyl bromide was condensed with diethyl alkyl malonates to give diethyl-Δ^2-cyclopentenylethyl alkyl malonates.

Δ^2-Cyclopentenyl Alkyl Acetic Acids and Δ^2-Cyclopentenylethyl Alkyl Acetic Acids.—The malonic esters were saponified with alcoholic potassium hydroxide as previously described and the potassium salt was obtained by evaporation to dryness. It was then dissolved in water and added to excess of concd. hydrochloric acid. Upon extraction with ether, evaporation of ether and heating for two hours at 160–165°, the monobasic acids were obtained. The yields were in the neighborhood of 90%.

Methyl-9-hydroxyhydnocarpate.—Δ^2-Cyclopentenylethyl bromide was converted into the corresponding Grignard in the usual way. This was then condensed with 8-aldehydo-octanoate in the proportion of 1 mole of aldehyde to 1 mole of Grignard reagent as shown by titration.[6] After working it up in the usual fashion, and after several careful fractional distillations, a constant boiling product was obtained; b. p. 177–179° at 2 mm.; n_D^{20}, 1.4720; d_4^{20}, 0.9874.

Anal. Calcd. for $C_{15}H_{30}O_3$: C, 71.91; H, 10.01. Found: C, 72.29; H, 10.70.

9-Hydroxy-*d,l*-Hydnocarpic Acid.—By saponification of the ester with alcoholic potassium hydroxide and working up in the manner described for the malonic acids, a solid acid was obtained which, upon crystallization from acetone, gave a constant m. p. of 62.0–62.8°.

Anal. Subs., 0.3688: 13.75 cc. of 0.1 *N* NaOH. Neut. equiv. Calcd. for $C_{14}H_{28}O_3$: 268.2. Found: 268.2.

Summary

1. A series of Δ^2-cyclopentenylethyl alkyl acetic acids has been prepared. Those members containing 16 to 18 carbon atoms showed a high bactericidal action toward B. *Leprae*.
2. Three of the higher members of the Δ^2-cyclopentenyl alkyl acetic acids have been prepared.
3. The synthesis of 9-hydroxy-*d,l*-hydnocarpic acid has been completed.

URBANA, ILLINOIS

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[6] (a) Noller with Adams, THIS JOURNAL, 48, 1074 (1926); (b) Davies and Adams, THIS JOURNAL, 50, 1749 (1928).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 22]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. III. FIRST CONTRIBUTION ON THE CARBON-CHLORINE BOND: THE RATE OF THE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

BY JAMES F. NORRIS AND AVERY A. MORTON[1]

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The influence of molecular structure on the reactivity of a chlorine atom in organic compounds is marked. This fact has been noted in a qualitative way since such compounds were studied. It is only recently, however, that attempts have been made to get a more definite conception of chemical reactivity by measuring quantitatively the relative rates at which the members of a series of analogous compounds react with a fixed reagent. Of the investigations in this field those that have the closest bearing on the work to be described have been published by Olivier,[2] who determined the rates at which benzyl chloride and certain of its derivatives react with ethyl alcohol, and by Conant and Kirner,[3] who have studied the rates at which the chlorine atom in certain compounds reacts with potassium iodide.

The investigation to be described in this and subsequent papers[4] was undertaken with the intention of studying the effect on the carbon-chlorine bond of a change in type of the halogen compound. For example, the replacement of two hydrogen atoms by one oxygen atom in an alkyl chloride leads to the formation of an acyl chloride (CH_3CH_2Cl and CH_3COCl). Such a change has a profound influence on the lability of the carbon-chlorine bond, and is worthy of detailed investigation. In the past the compounds studied comparatively have belonged to the same type, such as those formed by replacing by substituents one hydrogen in the benzene ring in benzyl chloride.

Since acetyl chloride is such a reactive compound it is difficult to measure the rate at which it reacts with another substance. The rate at which benzoyl chloride reacts with alcohol, however, can be measured. Its use as a type compound is advantageous, because the effect on the carbon-chlorine bond of replacing hydrogen in the benzene ring can be determined and can be compared with the effect of similar replacements on a com-

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[1] From the thesis of Avery A. Morton presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1924.

[2] Olivier, Rec. trav. *chim.*, 42, 773 (1923).

[3] Conant and Kirner, THIS JOURNAL, 46, 235 (1924).

[4] See Norris and Banta, THIS JOURNAL, 50, 1804 (1928); Norris and Blake, *ibid.*, 50, 1808 (1928); Norris and Gregory, *ibid.*, 50, 1813 (1928).

pound not containing oxygen. The simplest comparison would be between benzoyl chloride and benzyl chloride (C_6H_5COCl and $C_6H_5CH_2Cl$), but since there is such a wide difference between the reactivities of the two substances they cannot be studied under the same conditions. The replacement of one hydrogen atom linked to the methane carbon atom in benzyl chloride leads to a marked increase in the reactivity of the chlorine atom. The rate at which diphenylchloromethane reacts with ethyl alcohol can be measured under the same conditions as those used in the case of benzoyl chloride. As a consequence, the relative effects on the lability of the carbon–chlorine bond of one oxygen atom and of one hydrogen atom and one phenyl radical can be determined, and also the effect on this bond of similar replacements in the two type compounds. These effects are marked. The results lead to conclusions that have not been adequately recognized in the past in regard to the activation of atoms as the result of the replacement of hydrogen by other atoms or groups. The results obtained are described in the papers to which reference has been made.

This communication deals with a detailed study of the methods used in determining the velocity constant of the reaction between diphenylchloromethane and ethyl alcohol.

In the earlier part of the investigation the rate of the reaction was determined in the usual way by removing from time to time a sample of the reaction mixture and determining by titration the amount of hydrochloric acid formed. Although in the case of diphenylchloromethane the results were fairly accurate, the method was abandoned because the chloride was hydrolyzed to some extent when the analyses were made.

A method was developed that could be used for both the substituted alkyl chlorides and the acyl chlorides studied, because there was no opportunity for hydrolysis to take place. The reacting substances were placed in a conductivity cell and the resistance was measured as the reaction proceeded. The method has many advantages over one involving periodic analyses by the usual procedures. The reaction is carried out in a closed vessel and, consequently, there is no opportunity for contamination or extraneous changes which might be brought about during the process of analysis. The advantage which is most important when such reactive substances as acyl chlorides are studied comes from the fact that measurements can be made rapidly and at very short intervals. It was found possible to determine the velocity constant of a reaction that was complete in five minutes.

The results of the study of the applicability and accuracy of the method are described below. The work involved a redetermination of the conductivity of hydrochloric acid in ethyl alcohol, the effect of the influence of non-electrolytes on the conductivity, the influence of traces of water on the value of the velocity constant, the determination of the mechanism of the reaction, which was found to be a reversible one, and the development by Professor F. L. Hitchcock of the Department of Mathematics of the Massachusetts Institute of Technology of a new method of calculating the constant from the experimental results.

The velocity constants of the reaction at 25 and 0° were measured in order to calculate the temperature coefficient, which was useful in the comparison of the alkyl and acyl chloride studied. The rate of the reaction is markedly affected by a change in temperature; the rate nearly quadrupled for a rise of ten degrees.

Experimental Details

The measurements were made in conductivity cells similar to Washburn's type B,[5] but with the electrodes lightly platinized and one arm of each cell bent over and down into a mixing vessel from which the reactants could be transferred to the cell. Over a two year interval the cell constants did not vary more than 0.01% from the first determinations. A Leeds and Northrup bridge with extension coils and two resistance boxes containing Curtis coils of 100,000 and 1000 ohms, respectively, made by the same firm were used. The source of current was an improved form of induction coil known as the audio oscillator. This was tuned to a thousand cycles. A two stage amplifier connected in the manner described by Hall and Adams[6] enabled one to obtain a minimum of one part in five thousand very easily. Grounded shields were used to prevent any stray electrical effects. The thermostat and leads were also grounded. Every ordinary precaution, such as calibration, etc., was taken.

The alcohol was purified by first distilling it from dilute sulfuric acid to remove any amines. It was then refluxed over a mixture of calcium oxide and sodium hydroxide, after which two more refluxings over freshly ignited calcium oxide were carried out. Wherever corks were used they were covered with tin foil and suitable precautions were taken to insure the presence of dry air. The density at 25°, 0.78506, reported by the Bureau of Standards, Circular 19, was used as the criterion of pure alcohol. The alcohol used had this density within ±0.00002.

In the first six runs in absolute alcohol, the five runs in dilute alcohol and the two runs at zero degrees, the diphenylchloromethane was prepared by refluxing diphenylcarbinol with concentrated hydrochloric acid for at least two hours. The oil was then extracted with alcohol free ether, dried over anhydrous calcium chloride, and finally fractionally distilled in a vacuum. In runs seven to ten inclusive the compound was prepared by a method developed by Blake[4] in which hydrochloric acid was bubbled into a solution of the carbinol in specially purified petroleum ether in the presence of calcium chloride to remove water. After the old calcium chloride had been replaced twice with fresh material, the solution was filtered and the petroleum ether then removed by evacuating at room temperature. The purity was determined by refluxing duplicate samples of the chloride for two hours with an alcoholic solution of silver nitrate and comparing the amount of silver chloride formed with the amount theoretically possible.

The best determinations made of the conductance of hydrochloric acid in absolute alcohol at 25° are those of Goldschmidt.[7] His values were re-

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[5] Washburn, THIS JOURNAL, 38, 2431 (1916).

[6] Hall and Adams, *ibid.*, 41, 1515 (1919).

[7] Goldschmidt, *Z. physik. Chem.*, 89, 129 (1914).

calculated into terms of moles per 1000 g. of ethyl alcohol, since it is easier to make up the reaction mixture on the basis of weight formality. No great error is made in our case if the weight formality is calculated by simply multiplying his volume concentration by the ratio of the weights of the alcohol in the two solutions. Thus a 0.1 formal solution by volume becomes (1000 X 0.1)/785.06 or 0.12738 formal solution by weight. The specific conductance is calculated by the usual formula. Table I gives the original data with the recalculated values.

TABLE I

SPECIFIC CONDUCTANCE OF ETHYL ALCOHOL

Moles HCl per 1000 g. of C_2H_5OH. Temp., 25°

Vol., liters	Weight formality	Molecular conductance	$\bar{L} \times 10^3$
10	0.12738	35.0	3.50
20	.06369	40.4	2.02
40	.03185	46.3	1.158
80	.01593	52.7	0.659
160	.00796	59.0	.369
320	.00398	65.3	.204
640	.00199	70.4	.110
1280	.00099	74.2	.058
2560	.00050	76.9	.003

These values were checked with good agreement by solutions of hydrochloric acid in ethyl alcohol which were made up on the basis of weight formality. The specific conductance was plotted against weight formality so that the concentration of hydrochloric acid could be determined at any time from the conductivity measurement.

In order to obtain accurate results it is necessary to take into account the presence of a non-electrolyte in the solution. At the beginning of the reaction diphenylchloromethane and at the end the diphenylmethylethyl ether is present. Both of these lower the conductivity of hydrochloric acid in ethyl alcohol and it is therefore necessary to obtain some idea of the magnitude of this correction. A number of determinations were made with benzene, chlorobenzene, bromobenzene, naphthalene, dibromobenzene, diphenyl, diphenylmethane and naphthylphenylmethane as non-electrolytes. For the purposes of this work, that is, up to 0.12 formal, the percentage lowering of the specific conductivity for a fixed concentration of a given non-electrolyte with varying concentrations of hydrochloric acid is constant. On the other hand with a fixed concentration of hydrochloric acid the percentage lowering is directly proportional to the concentration of a given non-electrolyte. The effect of one non-electrolyte was not, however, the same as that of another. The differences between the various non-electrolytes could not be accurately related either to viscosities or molecular volumes. Table II shows the data for molecular volume and percentage lowering of the specific conductivity at 0.1 weight formal concentration. Where densities are not recorded In the literature they were determined. Measurement of the density of a solid at 25° was made by the molecular solution volume method of Traube.[8]

TABLE II

PERCENTAGE LOWERING OF SPECIFIC CONDUCTIVITY OF HYDROCHLORIC ACID IN ETHYL ALCOHOL PRODUCED BY NON-ELECTROLYTES

Concentration of HCl up to 0.12 moles and of non-electrolyte up to 0.1 mole per 1000 g. of ethyl alcohol. Temperature, 25.0°.

Non-electrolyte	Density	Molecular weight	Molecular volume	Lowering, %
Benzene	0.876	78.08	89.13	1.42
Chlorobenzene	1.104	112.5	102.0	1.64
Bromobenzene	1.561	157.0	105.0	2.05
Naphthalene	1.077	128.1	118.9	2.51
Dibromobenzene	2.022	235.9	116.6	2.64
Diphenyl	1.043	154.1	147.8	2.91
Diphenylmethane	1.006	168.2	167.3	3.15
Naphthylphenylmethane	1.129	218.2	193.3	3.91

As a rough approximation molecular volumes were used and a lowering of 3.2% in a 0.1 formal solution of diphenylchloromethane was chosen as an empirical value for the correction. It is probably not far from being the correct value. It was applied by means of the equation $\overline{L}_c = \overline{L}_0\ 100/(100-32f)$ where $\overline{L}_c$ is the corrected and $\overline{L}_0$ the observed specific conductance and f is the weight formality.

When the equation for a monomolecular irreversible reaction was applied it was found that the velocity constant was constant for about the first quarter of the run and then gradually became lower. Such an effect also occurs when the velocity is measured by titrating the hydrochloric acid. The most likely cause is that the reaction is reversible. A simple equation was developed by Hitchcock and Robinson[9] for the special case. The differential form of this equation is $dy/dt = k_1(X_0-y) - k_2y_2$, where y is the concentration of hydrochloric acid or diphenylmethylethyl ether formed; t is the time, X_0 equals the initial concentration of diphenylchloromethane and k_1 and k_2 are the velocity constants in the forward and reverse directions, respectively. Upon integration this equation becomes

$$k_2 = \frac{1}{t}\frac{2.303}{b + y_\propto}\left(\log\frac{b+y}{y-y} - \log\frac{b}{y_\infty}\right)$$

where $b = (X_0Y_\infty)/(X_0-y_\infty)$ and y_∞ = concentration of hydrochloric acid at infinite time; k_1 is then obtained by the equation $k_1 = k_2(y\alpha^2)/(x_0-y_\infty)$.

The data given in Table III are for the eighth run. The first column

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[8] Traube, *Ahren's* Vortrage, 4,255 (1899).

[9] Hitchcock and Robinson, "Differential Equations in Applied Chemistry," p. 52, John Wiley and Sons, Inc., 1923.

gives the corrected time. This correction was necessary because of the time required to mix the samples and bring the mixture to constant temperature. The maximum correction in any run was 1.3 minutes for this. In most of the runs it was much less. The second column is the specific conductance corrected for the concentration of non-electrolyte; the third column is $k_2 \times 10^5$; the fifth column is $k_1 \times 10^5$ as calculated by the reversible equation. The last column contains the calculation of k_1 on the basis of a monomolecular reaction only.

TABLE III

VELOCITY CONSTANTS FOR THE REVERSIBLE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

Temperature = 25 ± 0.01°. **Cell constant** = 1.0080. **Time in minutes. Formality of diphenylchloromethane** 89.80% **pure** = 0.07060. **Zero time correction** = +0.05 **min.**

Corr. time, min.	$\bar{L} \times 10^6$	Concd. HCl $\times 10^5$	$k_2 \times 10^5$	$k_1 \times 10^5$	$k_1 \times 10^5$
3.6	49	81	274	318	323
6.1	76	129	254	296	302
10.1	119	213	258	300	300
16.1	178	337	256	298	302
20.1	212	414	256	298	299
32.1	312	654	260	302	300
38.1	359	771	260	302	302
56.1	483	1095	256	298	299
84.1	654	1580	258	300	300
383.0	1599	4772	258	300	...
447.0	1707	5175	263	306	...
508 0	1785	5468	265	308	...
1205.0	2073	6576	268	312	...
1693.0	2096	6656	265	308	...
2703.0	2100	6678	...	...	...

x_0 = 0.0760. y_∞ = 0.06678. b = 1.234. **Reversible equation** k_1 = 0.00301. k_2 = 0.00259. **Monomolecular equation** k_1 = 0.00302.

Ten runs were made in absolute alcohol with diphenylchloromethane of varied purity and concentration. The results for these runs are given in Table IV.

The constants given for each run calculated from the equation for a reversible reaction are the average for about twelve observations during the course of the reaction. These observations generally agreed within less than 1% of the average and were never more than 3% from the average. The constants calculated from the equation for a first order reaction are based on observations up to approximately 25% conversion.

The very first observation made, usually within a minute after mixing, and the final observations, when the solution had been standing for twenty hours or more in the cell, were not of course within such accuracy but were generally within 10% of the average.

TABLE IV

VELOCITY CONSTANTS FROM THE REVERSIBLE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

Temperature, 25 ± 0.01°

Run No.	Diphenylchloromethane Concn.	Purity	Final conversion, %	Reversible equation $k_1 \times 10^5$	$k_2 \times 10^4$	Monomolecular equation $k_1 \times 10^5$
1	0.09790	97.75	94.1	310	21	302
2	.10008	97.75	92.6	307	27	306
3	,08808	97.80	87.1	268	52	266
4	.02618	97.80	84.3	261	230	259
5	.09680	96.56	93.4	304	23	304
6	.13925	96.56	93.8	304	15	304
7	.06470	89.86	94.0	300	31	299
8	.07060	89.86	94.6	301	26	302
9	.10667	99.98	86.4	277	48	276
10	.11330	99.98	89.6	281	37	280
			Average	291	51	290

The runs were made in pairs with different concentrations of diphenylchloromethane in each. The constants are nearly identical for each pair of runs. We cannot therefore see any effect due to a difference in concentration. Varying degrees of purity of the diphenylchloromethane cannot be said to have any effect since runs 7 and 8 where the material was only 89.56% pure are very close to runs 5 and 6 where the purity was 96.56%. A variation therefore may be due to impurities in the alcohol.

The most likely impurity in the ethyl alcohol is water. Accordingly five runs were made with different concentrations of water. The conductivity of hydrochloric acid in mixtures of water and alcohol was taken from Goldschmidt's[7] data. It was recalculated on a basis of weight formality as was done with the absolute alcohol. The correction for the presence of a non-electrolyte was assumed to be the same. Table V gives the results of these five runs.

TABLE V

THE EFFECT OR WATER ON THE VELOCITY CONSTANT OR THB REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL

Temperature, 25 ± 0.01°

No.	Water by weight, %	Formality of water	Formality of $(C_6H_5)_2C(H)Cl$	$k_1 \times 10^5$	$k_2 \times 10^4$
	0	0	....	291	51
11	0.15	0.0834	0.0990	316	26
12	.58	.3206	.1191	358	12
13	1.07	.5896	.1065	407	9
14	2.39	1.3258	.1242	532	15
15	7.19	3.989	.0815	1150	68

Good constants were obtained in all of these runs except in the case of number 15. The constants for that run increased continuously from the start. Near the end of the reaction it was nearly five times as large as at the beginning. The slope of the curve would lead one to suspect that the reaction between water and diphenylchloromethane proceeds simultaneously with that between ethyl alcohol and diphenylchloromethane. The value recorded here is an average for the first 40% of the run. These results show clearly that the presence of water has a marked effect. It is not, however, sufficient to account for all of the error. From 0% of water to 0.15% by weight, assuming that it is a straight line function, a change of 0.017 of water changes the k by 1.8. This would correspond to a change in the density of 0.00003, an amount which is detectable. If it is not a straight line function then the curve would tend to become more and more nearly parallel to the axis on which the value for the constant is plotted. The nearer the alcohol approached the absolute purity, the greater would be the change. In such a case the lowest value for the constant would be the more nearly correct. At this portion of a curve where concentration of water is plotted against the value for k, there seems to be a departure from the straight line. It is not possible, however, with the present data to say that the variation in the value of k for the first ten runs is positively due to traces of water.

The constant in the reverse direction is not nearly so accurate as the one in the forward direction. A consideration of the equation shows why this must be true, for the amount of hydrochloric acid present is very small in the early part of the run and this amount in the equation is squared.

Attempts to verify experimentally the calculated value were unsuccessful because of the high velocity. The reversibility of the reaction was shown however, by passing hydrochloric acid into a solution of the diphenylmethylethyl ether dissolved in a mixture of dry benzene and petroleum ether. Calcium chloride was then added to remove the ethyl alcohol formed. Distillation of the compound in a vacuum gave a product which analyzed 98.6% diphenylchloromethane.

For simplicity, a measurement of reaction velocity by a physical method is much to be preferred over a chemical one. The results in this case were very satisfactory but it was thought well to check the method by titrating the acid formed with sodium hydroxide and phenolphthalein as an indicator. A sample was removed from the reaction vessel, run into ice cold water, treated with a definite volume of cold carbon disulfide to remove the cloudiness from the precipitated organic compound and titrated with alkali. All ordinary precautions were made to stop the reaction and hasten the titration. The value for the first quarter of the run after making suitable corrections from blank experiments was 319×10^{-5} for k_1. This is 11% higher than the average obtained from the conductivity runs. The difference is believed to be due to the necessary presence of water in the reaction, which is largely avoided in the conductivity measurements.

Two runs were made at zero degrees with absolute alcohol. The thermostat for this was a glass bottle filled with cracked ice and water and surrounded with asbestos magnesia packing. Partington's[10] data for the conductance of hydrochloric acid in absolute alcohol at zero degrees were used. The values were converted to weight formality and the corrections for non-electrolyte were assumed to be the same as at 25°. The density of the alcohol was 0.8064 obtained by extrapolating the values given by the Bureau of Standards. The order of magnitude of k can be considered as the only significant value. Table VI below summarizes these two experiments.

TABLE VI

VELOCITY CONSTANT OR THE REACTION BETWEEN DIPHENYLCHLOROMETHANE AND ETHYL ALCOHOL AT 0°

No. of run	Concn.	Purity	$k_1 \times 10^5$
16	0.07745	99.98	10.4
17	.05502	99.98	11.3

By means of the equation $\log k_2/k_1 = A(T_2-T_1)/(T \times T_2)$ we obtain a value for A of 4630 as the temperature coefficient.

Summary

1. A method was developed for the determination of the velocity constants of the reaction between diphenylchloromethane and ethyl alcohol based on the measurement of the electrical conductivity of the solution as the reaction proceeded.

2. The reaction between diphenylchloromethane and ethyl alcohol was found to be reversible.

3. A new method has been developed for calculating the velocity constants of reversible reactions.

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[10] Partington, *J. Chem. Soc.*, 99, 1937 (1911).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO, 23]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. IV. SECOND CONTRIBUTION ON THE CARBON–CHLORINE BOND: THE RATES OF THE REACTIONS OF CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE WITH ETHYL ALCOHOL AND WITH ISOPROPYL ALCOHOL[1]

BY JAMES F. NORRIS AND CLIFFORD BANTA

RECEIVED APRIL 9, 1928 PUBLISHED JUNE 5, 1928

In this paper and the one by Norris and Blake[2] which follows are recorded the results of the determinations of the rates of the reactions between ethyl and isopropyl alcohols and certain derivatives of diphenylchloromethane. The investigation was undertaken to determine the effect of atoms and groups, and their positions relative to the carbon–chlorine bond, on the readiness with which the chlorine atom reacts with a fixed reagent under fixed conditions.

The results show that the lability of the chlorine atom as measured by the velocity constants of the reactions is markedly affected. The value of the constants varied between 0.01 and 1200 times that of the constant of the reaction between alcohol and the original molecule into which the substituents were introduced.

The velocity constants were determined in the way described in detail in the paper by Norris and Morton.[3]

In Table I are given the relative values of the constants observed by Banta and by Blake.

TABLE I

RELATIVE VELOCITY CONSTANTS OF THE REACTIONS BETWEEN ETHYL ALCOHOL AND CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE

Temperature 25.0°. Concentration of chloride approximately 0.1 formal by weight. Time in minutes.

Substituent	Relative values of constants	Substituent	Relative values of constants	Substituent	Relative values of constants
No substituent	1	*p*-Methyl	16.2	o-Methoxy	93
o-Chloro	0.01	*p,p'*-Dichloro	0.15	p-Methoxy	1200 (?)
m-Chloro	.045	*p,p'*-Dimethyl	413	*p*-Phenoxy	31.6
p-Chloro	.42	p-Ethyl	20.9	a-Naphthyl	7.2
o-Methyl	2 9	*p*-Bromo	0.33	Benzylphenylchloromethane	0.0004
m-Methyl	2.1	p-Phenyl	12.8		

The following conclusions can be drawn from the values given in the table.

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[1] From the thesis of Clifford Banta presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1922.

[2] Norris and Blake, THIS JOURNAL, 50, 1808 (1928).

[3] Norris and Morton, *ibid.*, 50, 1795 (1928).

(1) The influence on the activation of the carbon-chlorine hond is not in accord with the orienting effect of the substituent; chlorine decreases and methyl increases reactivity.

(2) Of the substituents studied only chlorine and bromine decreased reactivity.

(3) The groups that increased reactivity had their greatest effect when in the para position. For example, the relative velocity constants of the o-methyl and *p*-methyl derivatives were 2.9 and 16.2.

(4) Chlorine, which reduced reactivity, was most effective in the ortho position, the relative values of the ortho and para derivatives being 0.01 and 0.42.

(5) It appears from (3) and (4) above that reactivity is affected by the nature of the group and its position. The effect of the presence of a group in the ortho position is to reduce reactivity. If the atom or group also reduces reactivity the two effects work in the same direction; if the atom or group increases reactivity the effects are opposed.

(6) The groups that increase reactivity fall into the following series when para compounds are considered, the most effective being placed first: CH_3O, C_6H_5O, C_2H_5, CH_3, C_6H_5 and $C_{10}H_7$.

(7) Bromine like chlorine decreased reactivity and was more effective.

(8) A comparison of the relative velocity constant of benzylphenylchloromethane, 0.0004, with that of p-tolylphenylchloromethane, 16.2, leads to an important conclusion. In one compound $C_6H_5CH_2$- replaces $CH_3C_6H_4$- in the other. The relative positivity of these radicals as measured by their effect on the ionization constants of the corresponding acids, $C_6H_5CH_2COOH$ (5.4×10^{-5}) and $CH_3C_6H_4COOH$ (4.5×10^{-5}), are approximately the same. It follows, therefore, that the influence of a radical on the electrolytic ionization of an acid containing the radical is not a measure of the influence of the radical on the activation of the atoms within a molecule in which it is present. This conclusion is significant in that the degree of ionization is related to the equilibrium attained in a reaction, whereas reactivity is measured by the rates at which the reaction proceeds.

(9) A comparison of the results with those obtained by Olivier[4] in the study of the rates of the reactions at 83° between an aqueous solution of ethyl alcohol and certain derivatives of benzyl chloride shows that the effects of the introduction of the substituents into benzyl chloride and into diphenylchloromethane are similar. In the case of the methyl derivatives of benzyl chloride the relative velocity constants of the ortho, meta and para compounds are, respectively, 4.84, 1.39 and 10.6; in the case of the analogous derivatives of diphenylchloromethane the relative constants are 2.9, 2.1 and 16.2. For the corresponding chloro derivatives the values are,

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[4] Olivier, *Rec. trav. china.*, 42, 773 (1923).

respectively, 0.355, 0.237, 0.62 and 0.01, 0.045, 0.42. In both cases methyl increases and chlorine decreases reactivity but the effect of the halogen is greater in the case of the diphenylchloromethane derivative. In both cases bromine has a greater effect than chlorine.

(10) A comparison of the relative velocity constants of *p*-chlorodiphenylchloromethane (0.42) and *p,p'*-dichlorodiphenylchloromethane (0.15) and of the corresponding methyl derivatives (16.2 and 413) show that the constant of the disubstituted derivative is of the order of the square of the constant of the mono derivative; in the case of chlorine, which depresses reactivity, the value is slightly less than the square and in the case of methyl, which increases reactivity, the value is greater.

(11) The velocity constant of the reaction between *iso*propyl alcohol and diphenylchloromethane was determined. The value obtained was 11% of that of the reaction with ethyl alcohol. In the case of *p,p'*-dichlorodiphenylchloromethane the velocity with isopropyl alcohol was 15% of that with ethyl alcohol. These values serve to compare the relative lability of the hydrogen of the hydroxyl group in ethyl alcohol and in *iso*propyl alcohol. A previous determination of this value based on the study of the reaction between these alcohols and p-nitrobenzoyl chloride in ethereal solution gave 11.7%.[5]

Additional conclusions in regard to the effect of substituents on the reactivity of the carbon-chlorine bond in derivatives of diphenylchloromethane are given in the paper by Norris and Gregory: where the effect of the same substituents on the reactivity of the carbon–chlorine bond in derivatives of benzoyl chloride is considered.

TABLE II

VELOCITY CONSTANTS OF THE REVERSIBLE REACTION BETWEEN ETHYL ALCOHOL AND CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE

Concentration of chloride approximately 0.1 weight formal. Temperature 25.0°. Time in minutes.

Substituent	Constant	Average
No substituent	(0.00246), 0.00264, 0.00267	0.00266
o-Chloro	.0000253, 0.0000254	.0000254
p-Chloro	.00108, 0.00106	.00107
p-Methyl	.0417, 0.0430, 0.0453	.0433
p-Phenyl	.0379, 0.0375, 0.0333	.0362
p,p'-Dichloro	.000383, 0.000416	.00040
Benzylphenylchloromethane	.00000110, 0.00000114	.000000112

The following values were obtained when isopropyl alcohol was substituted for ethyl alcohol.

Diphenylchloromethane	0.000288, 0.000280	0.000284
p,p'-Dichloro	.0000580, 0.0000616	.0000598

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[5] Norris and Ashdown, THIS JOURNAL, 47, 837 (1925).

[6] Norris and Gregory, *ibid.*, 50, 1813 (1928).

Experimental Results

The work described in this paper was the first to be completed on the determination of the velocity constants of the reactions between diphenylchloromethane and its derivatives. The calculations of the constants based on a reaction of the first order showed that in certain cases the values decreased as the reaction proceeded. In the case of very rapid reactions satisfactory observations could be made only after a large percentage of the chloride had been converted. As the constants calculated in this way gave unreliable results the reaction was studied in detail by Morton,[3] who showed that it was reversible and applied a method of calculation that gave agreeing values of the constant. The results given in Table II are those obtained from the recalculation by Professor A. A. Morton of the experimental data of Dr. Banta.

Preparation and Properties of the Substances Used.—In all cases the derivatives of diphenylchloromethane were prepared by the action of hydrogen chloride on the corresponding carbinol dissolved in ether or benzene. This method was originally described by Montague,[7] who prepared a number of dreivatives of diphenylchloromethane.

When the reaction was complete the solutions were freed from acid, dried with calcium chloride and evaporated. If the chloride proved to be a solid it was recrystallized, usually from petroleum ether; if a liquid, it was distilled under diminished pressure. In the case of liquid chlorides that could not be distilled, the solutions in benzene or ether were thoroughly dried, evaporated in a current of dry air at room temperature to constant weight and analyzed. If the product so obtained proved to be deficient in chlorine the percentage purity was calculated from the analysis and taken into account in making up the solutions for the determination of the velocity constants. The largest variation from the theoretical amount of chlorine occurred in the case of *p*-bromodiphenylchloromethane, which contained 11.79 instead of 12.59% of the halogen. The product was accordingly 93.6% pure. It was shown by Morton[a] that the impurities introduced into diphenylchloromethane made by a procedure similar to that described here had little effect on the velocity constant, provided the actual weight of the chloride used was known.

TABLE III

PROPERTIES OF THE SUBSTANCES USED. COMPOUNDS MARKED WITH AN ASTERISK HAVE NOT BEEN DESCRIBED BEFORE

Compound or derivative	M. p. of corresponding carbinol, °C.	B. p., °C.	M. p., °C.	Side chain chlorine, % Theoretical	Found
Diphenylchloromethane	67–68	167 (16 mm.)	17–18	17.51	17.47, 17.50
p,p'-Dichloro	92–94	......	63	13.06	13.01, 12.98
p-Phenyl	93–96	......	*71–72.5	12.72	12.62, 12.60
p-Chloro	57–59	*172–173 (6 mm.)	....	14.96	14.86, 14.88
p-Methyl	51.5–53	*147–148 (2 mm.)	....	16.37	16.25, 16.22
o-Chloro	65	*Decomposed at 90	....	14.96	14.59, 14.54
Benzylphenyl	67	Decomposed	....	16.37	15.02, 15.01
p,p-Dimethyl	67–69	......	*41–43.5	15.37	14.04
p-Bromo	59–61	*188–191 (10 mm.)	....	12.59	11.77, 11.80

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[7] Montague, *Rec. trav. chim.*, **25,** 403 (1906); **24,** 115 (1905); **26,** 266 (1907); **27,** 327, 355 (1908); **31,** 311 (1912).

The method of Schulze[8] for the determination of side chain chlorine was used. In certain cases the time of refluxing the halide with the alcoholic solution of silver nitrate was increased to two hours. Experiments with *p*- and o-chlorodiphenylcarbinol showed that the halogen in the ring was not removed by the solution of silver nitrate.

The ethyl alcohol used in the determination of velocity constants was purified in the usual way and dried over lime. The density of the samples used varied from d_4^{25}, **0.78501** to **0.78511.** The isopropyl alcohol (from petroleum) was purified by the method of Lebo.[9] It boiled at 82.3–82.4°. The samples used varied in density from d_4^{25}, **0.7824** to **0.7821.**

Summary

1. The velocity constants of the reaction between ethyl alcohol and the following derivatives of diphenylchloromethane have been determined: o-chloro, p-chloro, *p,p'*-dichloro, p-bromo, p-methyl, p-phenyl. Similar constants for the reactions between ethyl alcohol and benzyl phenylchloromethane, *iso*propyl alcohol and diphenylchloromethane, and *iso*propyl alcohol and *p,p'*-dichlorodiphenylchloromethane have been determined.

2. The effect of substituents in diphenylchloromethane on the reactivity of the side chain halogen is marked. Halogen atoms depress reactivity, the greatest effect resulting from substitution in the ortho position. The methyl and phenyl radicals increase reactivity, the greatest effect resulting from substitution in the para position.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OR TECHNOLOGY, No. 24]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. V. THIRD CONTRIBUTION ON THE CARBON–CHLORINE BOND: THE RATES OF THE REACTIONS OF CERTAIN DERIVATIVES OF DIPHENYLCHLOROMETHANE WITH ETHYL ALCOHOL

BY JAMES F. NORRIS AND JOHN TWISS BLAKE[1]

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In this paper are reported the results of the determination of the rates at which nine derivatives of diphenylchloromethane react with ethyl alcohol. The compounds which had not been previously prepared were selected in such a way that the results could be used along with those obtained by Banta[2] in determining the effect of the position of a substituent on the reactivity of the carbon–chlorine bond.

In some of the compounds the chlorine atom was exceedingly labile.

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[8] Schulze, *Ber.*, 17, **1675 (1884).**

[9] Lebo, THIS JOURNAL, **43,1005 (1921).**

[1] From the thesis of John Twiss Blake presented in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, **1924.**

[2] Norris and Banta, THIS JOURNAL, 50, **1804 (1928).**

The determination of the very high reaction velocities was made possible only as a result of the use of the rapid method of measuring the concentration of the reacting substances by means of the conductivity of the solution. Even with this aid it was necessary to make observations toward the end of the reaction, and as a result the first order constant could not be calculated by using the usual formula. When the method of treating the results in the way described by Morton[3] was used satisfactory constants were obtained from the changes in concentration up to the point where over 80% of the substances had reacted.

Of the substituents studied the CH_3O and C_6H_5O groups in the para position were found to have the greatest effect in increasing the reactivity of the carbon–chlorine bond. The velocity constant of the reaction between ethyl alcohol and *p*-phenoxydiphenylchloromethane was 31.6 times that of diphenylchloromethane. The p-methoxy derivative contained such an active carbon–chlorine bond that the true velocity constant of the reaction between it and ethyl alcohol has not yet been determined. An examination of the reaction of the chloride in isopropyl alcohol at 0° indicates that the carbon–chlorine bond in *p*-methoxydiphenylchloromethane is over 1000 times as reactive as is the same bond in diphenylchloromethane. Both the p-phenoxy and the p-methoxy compounds contain chlorine atoms that are more reactive toward ethyl alcohol than the chlorine atom in benzoyl chloride. The constant of the reaction with p-phenoxydiphenylchloromethane is about 20 times that of the constant in the case of benzoyl chloride, both being determined at 25°. In these cases an oxygen atom singly linked to the ring in the para position has a greater effect on the carbon–chlorine bond than the same atom doubly linked to the carbon with which the chlorine is combined. These substitution products of an alkyl chloride are more reactive than benzoyl chloride.

When p-methoxydiphenylchloromethane in the form of drops is placed under cold water it is converted into the carbinol in less than one minute. Under the same conditions benzoyl chloride reacts very slowly. Both the *p*-methoxy and the p-phenoxy derivatives are colored. It is possible that molecular rearrangements have taken place and that the compounds do not have the structure assigned to them or are in equilibrium with quinoid forms.[4] It has been shown, however, that when the methoxy compound reacts with alcohol the chlorine atom is replaced and hydrochloric acid is formed in the normal way. The colored chloride gives the colorless carbinol when it reacts with water.

When the hydrogen of the benzene ring of diphenylchloromethane is replaced by either methyl or phenyl, the lability of the carbon–chlorine

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[3] Norris and Morton, THIS JOURNAL, 50, 1795 (1928).

[4] Bistrzycki and Herbst, *Ber.*, 36, 2335 (1903).

bond is increased. It was inferred from these facts that α-naphthylphenylchloromethane would react with alcohol more rapidly than does diphenylchloromethane. The constant of the former reaction was found to be about 7 times that of the latter.

The values of the velocity constants determined are given in Table I. The measurements were made in solutions less than 0.1 N. A fuller condensation of the effect of structure in the reactivity of the carbon-chlorine bond in the derivatives of diphenylchloromethane is given in the paper by Norris and Banta,[5] in which all the results are brought together.

TABLE I

FIRST ORDER VELOCITY CONSTANT OF THE REACTIONS BETWEEN ETHYL ALCOHOL AND CERTAIN DERIVATIVES OR DIPHENYLCHLOROMETHANE

Temperature, 25.0°. Time in minutes

Derivative of diphenylchloromethane	K	**Average** K
m-Chloro	0.0000583, 0.0000606, 0.0000590	0.0000593
p-Bromo	.000859, 0.000867, 0.000898, 0.000918	.000883
m-Methyl	.00545, 0.00563, 0.00563, 0.00544	.00554
o-Methyl	.00743, 0.00754, 0.00775, 0.00785	.00764
p-Ethyl	.0545, 0.0550, 0.0570, 0.0569	.0558
o-Methoxy	.251, 0.252, 0.239, 0.246	.247
p-Phenoxy	.846, 0.833, 0.842, 0.851	.843
p,*p*′-Dimethyl	1.09, 1.06, 1.16	1.10
α-Naphthylphenylchloromethane	0.0183, 0.0196, 0.0200	0.0193

Preparation and Properties of Compounds Used

A brief account of the methods by which the compounds used in the determination of velocity constants were prepared is given below. Details are indicated only in the case of compounds not heretofore described. Especial care was taken to have each compound free from structural isomers.

The derivatives of diphenylchloromethane were prepared from the corresponding carbinols by treatment of the latter, dissolved in petroleum ether and benzene, with hydrogen chloride. Anhydrous calcium chloride was placed in the solution to react with the water formed. After the solution was poured off from the solid, fresh calcium chloride was added and the treatment with hydrogen chloride repeated. The solution was filtered and evaporated at room temperature under diminished pressure. When the chloride was an oil the solution was evaporated to constant weight and the residue was then analyzed. Care had been taken to use solvents that left no residue on evaporation. The petroleum ether used was freed from unsaturated compounds by treatment with bromine, washing with alkali and subsequent distillation. The portion boiling between 35 and 60° was used. The compounds prepared in this way were obtained in a high degree of purity.

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[5] Norris and Banta, THIS JOURNAL, 50, 1804 (1928).

o-Methyldiphenylchloromethane.—o-Methyldiphenylcarbinol (m. p. 93°), prepared by the Grignard reaction from o-bromotoluene (b. p. 58–59° at 13 mm.) and benzaldehyde, was converted into the chloride in the way described above. The latter crystallizes in colorless plates (m. p. 40–40.5°) and is quite soluble in the usual solvents; Cl formed, 16.30 and 16.37%; calcd., 16.37%.

p-Methoxydiphenylchloromethane.—Fifteen grams of p-methoxybenzophenone (m. p. 62°) prepared from anisole and benzoyl chloride was reduced to the corresponding alcohol by refluxing with 10 g. of sodium hydroxide, 10 g. of zinc dust and 100 cc. of alcohol for two and one-half hours. The solution was filtered and poured into ice water. The solid after crystallization from dilute alcohol melted at 59–60"; yield, 10 g. The melting point of the compound prepared in other ways[6,7] is given as 58 and 60".

The carbinol was converted by means of hydrogen chloride into p-methoxydiphenylchloromethane. During its formation a reddish color developed which could not be removed by treatment of the solution with bone black. The chloride was obtained as a red oil which reacted rapidly with water. In less than one minute a sample of it was converted into the colorless carbinol. Analyses of the oil gave 15.23 and 15.18% chlorine; calcd., 15.24%.

p,p′-Dimethyldiphenylchloromethane.—p,p′-Dimethylbenzophenone (m. p. 92°) prepared from carbonyl chloride and toluene[8] was reduced in alcoholic solution with zinc and sodium hydroxide to the carbinol (m. p. 71"). The latter was converted by hydrogen chloride into p,p′-dimethylchloromethane, which crystallizes from petroleum ether in white prisms (m. p. 45–46°); Cl found, 15.35 and 15.39%; calcd., 15.37%.

p-Phenoxydiphenylchloromethane.—Ten grams of p-phenoxybenzophenone (m. p. 71°) prepared from diphenyloxide and benzoyl chloride was heated for two hours on a water-bath with 100 cc. of alcohol, 10 g. of sodium hydroxide and 10 g. of zinc dust. The filtered solution was poured into ice water. The colorless oil was extracted with ether and the solution dried. On long standing p-phenoxydiphenylcarbinol, which has not been described, crystallized in white rosets which melted at 75°.

The carbinol was converted by the usual procedure into the chloride, which crystallizes in needles possessing a pale orange color; m. p. 49–50°; Cl found, 12.00 and 11.96; calcd., 12.02%.

p-Ethylbenzophenone.—p-Ethylbenzophenone was prepared from ethylbenzene and benzoyl chloride.[10,11] After four fractionations the ketone boiled at 328–330°. Smith gives 330–332" as the boiling point and Vorlander gives 328°. A sample of the ketone gave on oxidation p-ethylbenzoic acid (m. p. 192').

p-Ethyldiphenylcarbinol has not been described. It was prepared from the ketone by the method outlined above and was obtained as an oil which was converted into white needles (m. p. 33°) when a solution of the oil in petroleum ether evaporated slowly.

p-Ethyldiphenylchloromethane which was prepared from the carbinol is a colorless liquid which boils at 122" (1–2 mm.) and shows a slight purple fluorescence. It did not solidify at −15°; Cl found, 14.92 and 14.97%; calcd., 15.37%.

o-Methoxydiphenylchloromethane.—o-Methoxybenzaldehyde (b. p. 241–242°) was prepared by a method similar to that of Clarke[12] from salicylic aldehyde and methyl sulfate. The aldehyde was converted into o-methoxydipheuylcarbinol (m. p. 139")

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[6] Busch and Leefhelm, J. prakt. *Chem.*, 77, 20 (1908).

[7] Cohen, *Rec. trav. chim.*, 38, 122 (1919).

[8] Ador and Crafts, *Ber.*, 10,2174 (1877).

[9] Kipper, *Ber.*, 38, 2492 (1905).

[10] Smith, *Ber.*, 24, 4029 (1891).

[11] Vorländer, *Ber*,, 44, 2462 (1911).

[12] H. T. Clarke, private communication.

through the use of the Grignard reaction.[13] The carbinol yielded *o*-methoxydiphenylchloromethane when treated with hydrogen chloride. The compound is a pale pink oil; Cl found, 15.14 and 15.10%; calcd., 15.24%.

α-Naphthylphenylchloromethane.—α-Naphthylphenyl ketone (m. p. 74°)[14] was reduced in the usual way to the carbinol (m. p. 85°). The latter yielded the chloride, which crystallized from ligroin in needles (m. p. 64–64.5°); Cl found, 13.97 and 14.01%; calcd., 14.08%.

***p*-Bromodiphenylchloromethane.**—It was found impossible to prepare in a pure condition p-bromodiphenylcarbinol by reducing the corresponding ketone. Apparently some of the halogen is removed during the reaction. The carbinol was prepared with a good yield from *p*-bromobenzaldehyde by the Grignard reaction. The compound as crystallized from dilute alcohol melted at 63°. It was converted into *p*-bromodiphenylchloromethane, which proved to be a colorless oil; Cl found, 12.53 and 12.57%; calcd., 12.59%.

***m*-Methyldiphenylchloromethane.**—*m*-Bromotoluene[15] (b. p. 183–184°) was used with benzaldehyde to prepare m-methyldiphenylcarbinol (m. p. 52°). The melting point agrees with that obtained with the product formed by reducing *m*-methylbenzophenone with sodium amalgam[16], and not with that of a substance described as this compound by E. and O. Fischer.[17] m-Methyldiphenylchloromethane prepared from the carbinol is a colorless oil; Cl found, 16.20 and 16.22; calcd., 16.37%.

***m*-Chlorodiphenylchloromethane.**—*m*-Chlorobenzoyl chloride was prepared by the method of Hope and Riley.[18] The crude product was distilled at 10 mm. pressure and the fraction boiling below 100° was fractionated four times at atmospheric pressure. The chloride boiled at 224–227°. Hantzsch[19] gives the boiling point as 225°. The compound was used in making m-chlorobenzophenone (m. p. 81°), which was reduced to the carbinol (m. p. 39–40°) in the usual way. Koopal[20] gives 40° as the melting point.

m-Chlorodiphenylchloromethane is a colorless oil that did not solidify at −10°; Cl found, 14.80 and 14.87%; calcd., 14.96%.

The ethyl alcohol used had the specific gravity 0.78506_{4}^{25}, which agrees with the value given by the Bureau of Standards.

Summary

1. The properties and methods for the preparation of the following new derivatives of diphenylchloromethane are described: *o*-CH_3, *m*-CH_3, *o*-CH_3O, *p*-CH_3O, *p,p*-$(CH_3)_2$, *p*-C_6H_5O, *p*-C_2H_5, *m*-Cl and p-Br. α-Naphthylphenylchloromethane is also described.

2. The first order velocity constants of the reactions between ethyl alcohol and the chlorides listed above have been determined.

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[13] Stoermer and Friderici, *Ber.*, 41, 332 (1908).

[14] Elbs, *J. prakt. Chem.*, [2] 35, 502 (1887).

[15] Bigelow, THIS JOURNAL, 44, 2012 (1922).

[16] Montagne and Charante, *Rec. trav. chim.*, 31, 348 (1912).

[17] E. and O. Fischer, *Ann.*, 194, 265 (1878).

[18] Hope and Riley, *J. Chem. Soc.*, 121, 2515 (1922).

[19] Hantzsch, *Ber.*, 24, 57 (1891).

[20] Koopal, *Rec. trav. chim.*, 34, 115 (1915).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OR ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 25]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. VI. FOURTH CONTRIBUTION ON THE CARBON–CHLORINE BOND: THE RATES OF THE REACTIONS OF BENZOYL CHLORIDE AND CERTAIN OF ITS DERIVATIVES WITH ISOPROPYL ALCOHOL

BY JAMES F. NORRIS AND DWIGHT V. GREGORY[1]

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In the first investigation of the relative reactivities of the carbon–chlorine bond in acyl chlorides, the rates at which these chlorides react with isopropyl alcohol were determined. This alcohol was selected because the reactivity of its hydrogen atom is low and as a consequence the reaction velocities are much smaller and easier to measure than the velocities of the corresponding reactions with ethyl alcohol. Certain difficulties were encountered in making very accurate measurements and the later work with the acyl chlorides was carried out with ethyl alcohol at 0°. The results obtained with this alcohol, to be published later, show that the relative rates with which the several acyl chlorides react as measured by either isopropyl alcohol or ethyl alcohol are approximately the same.

The velocities were measured of the reactions between the acyl chlorides and *iso*propyl alcohol by determining from time to time the amount of hydrochloric acid formed. The latter was measured by observing the conductivity of the solution. It was necessary to determine the conductance of solutions of hydrochloric acid in *iso*propyl alcohol at different concentrations. It was found impossible to get results of the highest degree of accuracy because there was a slow reaction between the acid and the alcohol at 25°. The error introduced in this way was shown to affect the value of the velocity constant to not more than 2%. Other sources of error were unavoidable but it is safe to say that the results are accurate to within less than 10%. The results are valuable as they can be used in making comparisons when such a possible error is of no great significance. The constants determined are shown in Table I.

The results show that the halogens increase and the methyl group decreases the reactivity of the carbon–chlorine bond. The effect of these substituents in benzoyl chloride is the reverse of their effect in diphenylchloromethane.[2] This is a significant fact. The results obtained from the study of the reaction of a large number of acyl and substituted alkyl chlorides with ethyl alcohol lead to the conclusion that the activation of an atom in a given compound produced as the result of the substitution of

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[1] From the thesis of Dwight V. Gregory presented in partial fulfilment of the requirements for the degree of Master of Science, 1922.

[2] Norris and Banta, THIS JOURNAL, 50, 1804 (1928).

TABLE I

FIRST ORDER VELOCITY CONSTANTS OF THE REACTIONS OF CERTAIN ACYL CHLORIDES WITH *ISO*PROPYL ALCOHOL

Temp., 25.0°. Concentration approximately 0.1 Formal per 1000 g.

Acyl chloride	*K*	*K*	Average	Ratio of constant to that of benzoyl chloride
Benzoyl	0.00371	0.00360	0.00365	1
p-Chloro benzoyl	.00550	.00569	.00559	1.53
p-Bromo benzoyl	.00645	.00655	.00650	1.78
p-Iodo benzoyl	.00546	.00511	.00528	1.26
o-Nitro	.00682	.00706	,00694	1.90
p-Nitro benzoyl	.033	.040	.036	10.0
p-Methyl benzoyl	.00240	.00229	.00235	0.64

hydrogen by another atom or group is determined by the nature not only of the substituent but the molecule modified. When the negative chlorine atom replaces hydrogen in benzoyl chloride, the effect of the negative oxygen atom in the chloride takes part in the changed reactivity of the acyl chloride. The lability of the acyl carbon–chlorine bond is increased. On the other hand, when the same negative atom is introduced into diphenylchloromethane in which the oxygen atom of the acyl chloride is replaced by the more positive hydrogen atom and the phenyl radical, the combined effect leads to decreased reactivity of the analogous carbon–chlorine bond. In the case of the introduction of the positive methyl radical into the two molecules the effects are reversed. It appears, therefore, that the lability of the carbon–chlorine bond studied is increased when either a negative atom or group (Cl or NO_2) is introduced into a molecule containing negative atoms or when a positive group (CH_3, C_6H_5, etc.) is introduced into a molecule containing positive atoms or groups. The lability of the carbon–chlorine bond is decreased when a negative substituent is introduced into the molecule containing positive atoms or a positive group is introduced into a molecule containing negative atoms and groups. These conclusions hold in regard to a large number of derivatives of diphenylchloromethane and of benzoyl chloride.

In both series of compounds bromine is more effective than chlorine. The former depresses reactivity more than the latter in the substituted alkyl chloride and increases reactivity more than chlorine in the acyl chloride.

Experimental Details

The difficulty encountered in an attempt to determine accurately the conductivity of hydrochloric acid of different concentrations in *iso*propyl alcohol was traced to the fact that the resistance of the solutions changed slowly. Staud in this Laboratory showed that a solution of 0.0756 N hydrochloric acid changes in resistance equivalent to a change in concentration at the rate of 0.4% per hour and that one of 0.006 *N* changed at the rate of 2% per hour. In order to keep the error due to this fact as low as possible, the values of all velocity constants were calculated from observations made at times of less than one hour. In this way this error was less than 2%.

A number of check determinations of the conductivity of the acid in *iso*propyl alcohol were made at different concentrations and the results plotted. The curves diiered by 3% at 0.1 N and 4% at 0.001 N. The values of the constants are affected by this uncertainty. New data are being determined and the results will be published later.

All observed conductivities were corrected for the effect of the non-electrolyte present. It was shown that 0.1 N propyl benzoate lowers the conductivity of hydrochloric acid 6.1%. The lowering was independent of the strength of the acid within the limits of concentration used and was proportional to the strength of the ester. These results were used in the experiments with benzoyl chloride. In the case of the other compounds a further correction was made based on change in the non-electrolyte.

The values of the constants were calculated in the usual way from observations made up to 30% conversion. Up to this point the value of the term log $(X_0)/(X_0-X)$ in the equation for a first order reaction divided by the time remained a constant. A time correction was avoided by taking as concentration at zero time the concentration observed after the reaction had proceeded for several minutes.

By limiting the observations to those obtained within one hour, the error caused by the reaction between hydrochloric acid and isopropyl alcohol was reduced to less than 0.4%.

The methods of preparation of the compounds used and the purity of the latter are indicated in Table II.

TABLE II

PREPARATION AND PROPERTIES OF COMPOUNDS STUDIED

The melting points are uncorrected

Benzoyl chloride....	Fractionated, b. p. 197.2–197.3°. Analysis, 99.9–100.25%.
p-Chloro chloride....	From acid, m. p. 239°. Chloride fract. 3 times, dim. pressure. Analysis, 100.4–100.1%.
p-Bromo chloride....	From acid, m. p. 250–252°. Chloride fract., dim. pressure. Analysis, 101.4 and 100%.
p-Iodo chloride......	From acid, m. p. 265–266°. Chloride fract., dim, pressure. Analysis, 101 and 102.7%.
o-Nitro chloride.....	Chloride fract., dim. pressure. Analysis, 100.6 and 99.5%.
p-Nitro chloride.....	From acid, m. p. 240°. Chloride fract., dim, pressure. Analysis, 100.2 and 100.3%.
p-Methyl chloride...	From acid, m. p. 179°. Chloride fract. 3 times. Analysis 99.9 and 99.3%.

The isopropyl alcohol was distilled several times from lime. Its density was 0.7843 $\frac{25°}{4°}$. The only accurate density available when this work was done was that obtained by Lebo[3]: $0.78556\,^{20^\circ}_{4^\circ}$. Later determinations by Brunel[4] gave the value $0.7808\,^{25^\circ}_{4^\circ}$.

Summary

1. First order velocity constants have been determined for the reactions between isopropyl alcohol and benzoyl chloride and the following derivatives of benzoyl chloride: p-chloro, p-bromo, p-iodo, o-nitro, *p*-nitro and *p*-methyl.

2. A comparison of the activating influence of substituents on the reactivity of the carbon–chlorine bond in derivatives of benzoyl chloride and of diphenylchloromethane shows that negative atoms (Cl, Br, NO_2) increase the lability of the bond in acyl chlorides and decrease the lability of the bond in derivatives of diphenylchloromethane. The positive methyl group increases reactivity in the acyl and decreases reactivity in the alkyl compounds.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA]

NITROGEN TRICHLORIDE AND UNSATURATED KETONES. II

BY GEORGE H. COLEMAN AND DAVID CRAIG[1]

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The reaction of nitrogen trichloride with benzalacetophenone[2] forms among other products 2-chloro-1-dichloro-amino-1,3-diphenylpropanone-3. The addition is probably to the —C=C— bond as in the corresponding reaction with the unsaturated hydrocarbons[3] and does not involve the carbonyl group.

The reaction has now been studied with benzalacetone. The products obtained with this compound are 2-chloro-1-dichloro-amino-1-phenylbutanone-3 (I), the dichloride of benzalacetone, ammonium chloride and a large amount of nitrogen gas. Product I was reduced by concentrated hydrochloric acid[4] to the corresponding amino chloro ketone II. If the reaction mixture containing I is allowed to stand for several days at room temperature, II will crystallize out as the hydrochloride. Its formation is no doubt due to the hydrochloric acid produced by the decomposition of

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[3] Lebo, THIS JOURNAL, 43, 1005 (1921).

[4] Brunel, *ibid.*, 45, 1336 (1923).

[1] This paper is an abstract of a part of the thesis submitted by David Craig in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the State University of Iowa.

[2] Coleman and Craig, THIS JOURNAL, 49, 2593 (1927).

[3] Coleman and Howells, *ibid.*, 45, 3084 (1923).

[4] The reducing action of hydrochloric acid on chloro-amines was reported by Berg. His best reference is Ann. *chim. phys.*, [7] 3, 338 (1894).

benzalacetone dichloride. Evidence regarding this decomposition is given in the Experimental Part. This is a more satisfactory method for obtaining the hydrochloride than the treatment with concentrated hydrochloric acid. It is interesting to note that the method may be applied to benzalacetophenone but is not as satisfactory for this compound as the concentrated hydrochloric acid method.

In proving the structure of II, its hydrochloride was reduced with sodium amalgam to the corresponding amino alcohol III. Several attempts to prepare this amino alcohol by other methods were not successful. Its isomer IV was therefore made from 2-amino-1-phenylbutanone-3 by reduction with sodium amalgam. The properties of the two compounds were quite different. Derivatives of both were prepared and analyzed and their molecular weights determined. The reactions for the addition and for the proof of structure of the product are as follows

$$C_6H_5CH{=}CHCOCH_3 + NCl_3 = C_6H_5CH(NCl_2)CH(Cl)COCH_3 \qquad (I)$$

$$C_6H_5CH(NCl_2)CH(Cl)COCH_3 + 2HCl = 2Cl_2 + C_6H_5CH(NH_2)CH(Cl)COCH_3 \qquad (II)$$

$$C_6H_5CH(NH_2)CH(Cl)COCH_3 + 4H = HCl + C_6H_5CH(NH_2)CH_2CH(OH)CH_3 \qquad (III)$$

$$C_6H_5CH_2CH(NH_2)COCH_3 + 2H = C_6H_5CH_2CH(NH_2)CH(OH)CH_3 \qquad (IV)$$

This addition is in agreement with other addition reactions of benzalacetone in which the negative part of the adding molecule attaches itself to the carbon atom farthest from the carbonyl group. Such reactions are those with amines,[5] *p*-toluenesulfinic acid[6] and cyanoacetic esters.[7]

The reaction of nitrogen trichloride with benzalacetone is more rapid than with benzalacetophenone under the same conditions. The yield of addition product obtained with benzalacetone is less and the amount of ammonium chloride greater.

Experimental Part

Nitrogen trichloride was prepared by the method described by Coleman and Noyes[8] with modifications as described by Coleman and Howells.[3]

Analysis of Nitrogen Trichloride Solutions.—Nitrogen trichloride reacts with hydrochloric acid to give ammonium chloride and chlorine. Probably the best method for analyzing nitrogen trichloride solutions utilizes this reaction. The reaction is reversible and the equilibrium adjusts itself very rapidly. However, by the removal of chlorine and the use of a large excess of hydrochloric acid, the reaction can be made to go to completion. It has been found necessary to make special provision for the removal of chlorine when working with the more concentrated solutions. Figure 1 illustrates a satisfactory apparatus for use in analyzing carbon tetrachloride solutions of nitrogen trichloride. C is a 40cc. test-tube half filled with concentrated hydrochloric acid. A is the reaction chamber made from 20-mm. glass tubing and is partially filled with glass beads. B is a side-arm test-tube which is connected to a water pump. For

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[5] Kohn, *Monatsh.*, 28, **423** (1907).

[6] Kohler and Reimer, *Am. Chem. Jour.*, 31,178 (1904).

[7] Kohler and Allen, THIS JOURNAL, 45,1987 (1923).

[8] Coleman and Noyes, *ibid.*, 43,2211 (1921).

the analysis of 2 cc. of carbon tetrachloride solution containing 3 gm. moles of nitrogen trichloride, 15 cc. of concentrated hydrochloric acid is introduced into A and 10 cc. into B. The sample is introduced into A from a pipet. A and B are then connected by means of a glass tube D and air is drawn through the apparatus rapidly enough so that the yellow color of chlorine and nitrogen trichloride disappears from the mixture in A in about two minutes. A is then heated to about 60° and the current of air continued until the carbon tetrachloride has been carried out of the apparatus. The contents of A and B are united and the amount of ammonia present is determined by distilling from an alkaline solution into 0.1 N acid. The mean error of this method is less than three parts per thousand.

Preparation of the Hydrochloride of 1-Amino-2-chloro-1-phenylbutanone-3.—One hundred and thirty grams of benzalacetone was dissolved in 500 cc. of dry carbon tetrachloride in a flask fitted with a mercury sealed stirrer and connected to a gasometer. The solution was cooled to −10° and 500 g. of a solution of nitrogen trichloride in carbon tetrachloride, containing 480 mg. moles of nitrogen trichloride, was added through a separatory funnel. The time of addition was about two hours. The evolution of nitrogen began when a small portion of the nitrogen trichloride had been added and continued for a short time after all of the solution had been run in. The reaction mixture was allowed to stand for about five hours. It was then filtered from ammonium chloride and allowed to stand at room temperature for three days. During this time the hydrochloride of 1-amino-2-chloro-1-phenylbutanone-3 crystallized out. The product was nearly pure. It was further purified by dissolving in the least possible amount of absolute alcohol and precipitating by the addition of dry ether. The compound melted with decomposition at 176–177°. The yield of the pure product was about 5%.

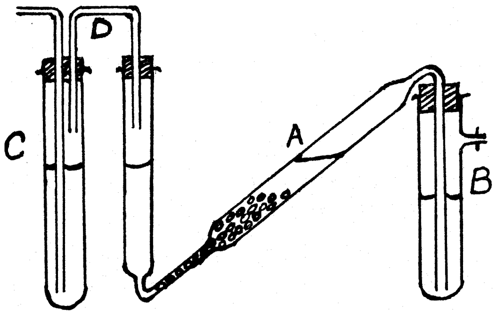

Fig. 1.

Anal. Subs., 0.0630: 28.30 cc. of 0.01 N HCl. Calcd. for $C_{10}H_{12}OClNHCl$: N, 5.99. Found: 6.29.

In another run the reaction mixture containing the dichloroamine was shaken with 50 cc. of concentrated hydrochloric acid for thirty minutes. The hydrochloride was obtained in the aqueous layer but was not isolated. By treating with benzoyl chloride according to the Schotten-Baumann procedure two products were obtained, the preparation of which from the pure hydrochloride is described in the next paragraph.

Benzoyl-1-amino-2-chloro-1-phenylbutanone-3.—This derivative was obtained in 70% yield by refluxing 0.5 g. of the hydrochloride with 0.5 cc. of benzoyl chloride in 10 cc. of benzene for several hours. After cooling and filtering the product was recrystallized from alcohol or from 140–160° boiling ligroin; m. p. 160–161° (uncorr.).

Anal. Subs., 0.0726: 24.40 cc. of 0.01 N HCl. Calcd. for $C_{17}H_{16}ClO_2N$: N, 4.64. Found: 4.71.

Subs., 0.2625: 8.53 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{17}H_{16}ClO_2N$: Cl, 11.74. Found: 11.54.

Benzoylation by the usual Schotten-Baumann procedure yielded the benzoyl derivative and a side product. The side product is almost insoluble in high boiling ligroin and melts with decomposition at 204° after being recrystallized from alcohol. It has about the same nitrogen content as the benzoyl derivative. Its structure was not determined.

Benzoyl-1-amino-1-phenylbutanol-3.—Since the benzoylation by means of the Schotten-Baumann procedure yielded two products, it was thought advisable to reduce the one which was most likely the true benzoyl derivative, that is, the one melting at 160–161°. The reduction was carried out in warm alcohol by means of sodium amalgam. Meanwhile the solution was kept slightly acid by means of 6 N hydrochloric acid. Most of the alcohol was then boiled out, the solution cooled and the product recrystallized from 140–160° boiling ligroin; m. p. 150–151° (uncorr.); yield, 67%.

Anal. Subs., 0.0494: 19.15 cc. of 0.01 N HCl. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: 5.43.

1-Amino-1-phenylbutanol-3.—Three grams of the pure hydrochloride of the amino chloro ketone was dissolved in 20 cc. of water and 189 g. of 2.5% sodium amalgam added in small pieces during an hour. The mixture was stirred and 6 N hydrochloric acid added rapidly enough to keep the solution slightly acid to litmus. The solution was poured from the mercury, made alkaline and extracted twice with ether. The ethereal solution was dried with sodium sulfate and evaporated to dryness on the steam-bath. On cooling 1.8 g. (85%) of 1-amino-1-phenylbutanol-3 was obtained. After two recrystallizations from 60–80° boiling ligroin, the product melted at 74–76' (uncorr.).

Anal. Subs., 0.0500, 0.0684: 5.91, 8.05 cc. of 0.05 N HCI. Calcd. for $C_{10}H_{15}ON$: N, 8.49. Found: 8.28, 8.25.

Acetylation Value.—Subs. 0.1842: 1.32 mg. equiv. of acetic anhydride. Calcd. for one NH_2: 1.00. Found: 1.18.

The acetate of this amino alcohol is probably soluble in water. At least under the experimental conditions it was saponified.[9]

Dibenzoyl Derivative of **1-Amino-1-phenylbutanol-3.**—This derivative was prepared by refluxing 0.3 g. of the amino alcohol with 0.54 cc. of benzoyl chloride and 5 cc. of xylene for two hours. On cooling 0.46 g. of the derivative was obtained. After recrystallizing from xylene the product melted at 139–141° (uncorr.). Benzene can be used in this procedure but because of its lower boiling point does not give as satisfactory results.

And. Subs., 0.0848: 22.90 cc. of 0.01 N HCI. Calcd. for $C_{24}H_{23}O_3N$: N, 3.76. Found: 3.79.

Molecular Weight Determination.—Subs., 0.0264: 0.4496 g. of camphor. Melting-point depression, 6.2'. Calcd. for $C_{24}H_{23}O_3N$: 373. Found: 379.

2-Amino-1-phenylbutanol-3.—Ten grams of the hydrochloride of 2-amino-1-phenylbutanone-3, prepared as described by Sonn,[10] was dissolved in water and 184 g. of 2.5% sodium amalgam added in small pieces and with stirring during an hour. The mixture was kept slightly acid with 6 *N* hydrochloric acid The solution was poured from the mercury, treated with Norit, filtered, and extracted with ether. It was then made alkaline and extracted twice with ether. The ether extractions were united and dried with sodium sulfate. After evaporating the ether on the steam-bath and cooling, 3.2 g. of the amino alcohol was obtained. It melted at 62–64° (uncorr.) after being recrystallized from 60–80° boiling ligroin.

Anal. Subs., 0.2086: 25.01 cc. of 0.05 N HCl. Calcd. for $C_{10}H_{15}ON$: N, 8.49. Pound: 8.40.

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[9] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 152. See also Coleman and Craig, ref. 2, p. 2595.

[10] Sonn, *Ber.*, **40**, 4666 (1907).

The hydrochloride of this compound was prepared and melted at 114–116° (uncorr.).

Benzoyl-2-amino-1-phenylbutanol-3.—This compound was obtained by refluxing a mixture of one mole of the amino alcohol with two moles of benzoyl chloride in benzene for three hours. It was also obtained by treating the amino alcohol according to the usual Schotten-Baumann procedure with benzoyl chloride. It melted at 177–179° (uncorr.) after two recrystallizations from 50% alcohol.

Anal. Subs., 0.0610: 22.70 cc. of 0.01 *N* HCl. Calcd. for $C_{17}H_{19}O_2N$: N, 5.20. Found: 5.21.

Molecular Weight Determination.—Subs., 0.0205, 0.0287: 0.3085, 0.3801 g. of camphor. Melting point depression, 9.4°, 11.0°. Calcd. for $C_{17}H_{19}O_2N$: 269. Found: 283, 274.

1-Chloro-1-phenyl-1-butenone-3.—The reaction of nitrogen trichloride with benzalacetone produced a large amount of benzalacetone dichloride. Since in the reaction mixture this compound was unstable toward heat and evolved hydrochloric acid, the solvent was evaporated at room temperature under reduced pressure. The yield of the dichloride obtained after recrystallizing the residue from alcohol was about 45% This slightly impure product on standing for several weeks began to decompose into hydrochloric acid and 1-chloro-1-phenyl-1-butenone-3. At the temperature of the water-bath this decomposition was complete in a few days. This monochloro unsaturated ketone was obtained by distilling the resulting oil under reduced pressure. It boils at 155–156° at 23 mm.

Anal. Subs., 0.5691: 32.25 cc. of 0.1 N $AgNO_3$. Calcd. for $C_{10}H_9ClO$: Cl, 19.65. Found: 20.09.

The oxime of this compound was prepared and analyzed. It was obtained in 65–70% yield, using hydroxylamine hydrochloride in alcohol–water solution in the presence of sodium acetate. It melted at 132–134° after being recrystallized from alcohol and its properties agree with those of the compound prepared by Goldschmidt.[11]

Benzalacetone dichloride may be obtained pure from the slightly impure product mentioned above by recrystallizing twice from alcohol. When so obtained it is stable at room temperature and can be distilled without decomposition at 159–160° at 21 mm. It melts at 93–94°.

Summary

1. Benzalacetone reacts with nitrogen trichloride in carbon tetrachloride solution to form among other products 2-chloro-1-dichloroamino-1-phenylbutanone-3. The addition is to the —C=C— bond and does not involve the carbonyl group. The addition product was reduced to the corresponding amino chloro ketone, the structure of which was established.

2. Benzalacetone dichloride, also formed in this reaction, decomposes in the reaction mixture at room temperature to 1-chloro-1-phenyl-1-butenone-3 and hydrochloric acid.

3. A method is given for the analysis of concentrated solutions of nitrogen trichloride.

IOWA CITY, IOWA

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[11] Goldschmidt, Ber., 28, 1532 (1895).

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, COLUMBIA UNIVERSITY, No. 571]

ESTERS OF ALPHA-TETRAHYDROFURFURYL ALCOHOL

BY J. E. ZANETTI

RECEIVED APRIL 25, 1928 PUBLISHED JUNE 5, 1928

As α-tetrahydrofurfuryl alcohol will shortly be available on a commercial scale from the catalytic reduction of furfural, it seemed desirable to investigate the properties of its esters, especially in regard to their stability as compared with those of a-furfuryl alcohol investigated some time ago in this Laboratory.[1]

The introduction of four hydrogen atoms in the furfuran ring produces a remarkable stability in the derivatives of the hydrogenated ring. For example, a-tetrahydrofurfuryl alcohol is a very stable compound, remaining colorless indefinitely, whereas a-furfuryl alcohol cannot be kept colorless even in the dark for more than a few weeks. The sensitivity of α-furfuryl alcohol to mineral acids is entirely absent from the hydrogenated alcohol and thus it becomes possible to use the ordinary esterification reactions for the preparation of its esters.

Methods of Preparation.—The use of hydrochloric acid gas and of sulfuric acid dissolved in the alcohol together with the acid whose ester is desired, the action of acid chlorides and anhydrides were all employed in the preparation of the esters described in this paper. The yields were uniformly good (80% or above) except in the preparation of the a-tetrahydrofurfuryl furoate by using sulfuric acid as a condensing agent, when much tar was obtained and only a 50% yield of the ester. This may be ascribed to the instability of the furfuran ring of the furoic acid.

Properties of the Esters.—The esters are all colorless liquids with very faint odors characteristic of the acids employed. The benzoate and the furoate are odorless. They are insoluble in water, with the exception of the acetate which is miscible with water in all proportions, but miscible with alcohol, ether and chloroform.

These esters are very stable and can be distilled under atmospheric pressure. If the boiling point is much over 200°, however, the samples thus distilled will color on standing, showing that some decomposition was initiated by the heating. For this reason the high boiling esters were distilled under reduced pressure. Thus purified they show no decomposition or coloration after two months with the exception of the furoate which, in common with all other esters of furoic acid, will color slightly on standing.

As a-tetrahydrofurfuryl furoate has a higher boiling point than α-furfwyl furoate, which is a dimorphous solid (m. p. 19.5 and 27.5°), it was thought that it might also be obtained in a crystalline form. This,

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[1] Zanetti, THIS JOURNAL, 47, 535 (1925); 47, 1452 (1925); Zanetti and Kerr, *ibid.*, 48, 794 (1926).

however, was not found to be the case. When cooled in a freezing mixture to −15°, the ester became a thick liquid of the consistency of glycerine. When cooled in a solid carbon dioxide–ether mixture, it assumed the consistency of Canada balsam and when finally cooled in liquid air it went suddenly and with great contraction in volume into a glassy solid without any trace of crystallization whatever. The solidified ester had the appearance of a block of shattered glass and even by keeping it at the temperature of liquid air for some time no crystals appeared. The benzoate and valerianate behaved similarly.

The physical constants and analyses of the esters prepared are given in Table I.

TABLE I

ESTERS OF α-TETRAHYDROFURFURYL ALCOHOL

Compound	B. p., °C.	Press., mm.	D_0^{20}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Acetate, $C_7H_{12}O_3$	194–195	753	1.061	58.33	58.57	8.33	8.71
					58.78		8.85
Propionate, $C_8H_{14}O_3$	204–207	756	1.044	60.79	60.36	8.86	8.92
	85–87	3			60.27		8.49
Butyrate, $C_9H_{16}O_3$	225–22b	759	1.012	62.79	62.61	9.30	9.57
	102–104	4			62.31		9.38
Valerianate, $C_{10}H_{18}O_3$	238–240	756	0.999	64.51	64.36	9.68	9.68
	97–99	2			64.25		9.78
Benzoate, $C_{12}H_{14}O_3$	300–302	750	1.137	69.90	69.25	6.99	6.94
	138-140	2			69.80		6.55
Furoate, $C_{11}H_{12}O_4$	136–138	3	1.194	60.60	60.39	6.06	6.06
					60.59		6.08

The writer is indebted to the Miner Laboratories for kindly supplying him with a-tetrahydrofurfuryl alcohol.

Summary

1. The acetate, propionate, butyrate, valerianate, benzoate and furoate of a-tetrahydrofurfuryl alcohol have been prepared and their properties reported.

NEW YORK, N. Y.

NOTE

Luminescence **of** Aliphatic **Grignard** Compounds.—The purpose of this note is to clear up a disagreement in which the writer had a share. In studying the luminescence of Grignard compounds in ether solution when reacting with oxygen, especially of aliphatic compounds, we find on the one hand Möller[1] recording light from ethylmagnesium bromide, propylmagnesium bromide, *iso*-amylmagnesium bromide and benzylmagnesium bromide; and Evans and Diepenhorst[2] reporting light from several

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[1] Möller, *Arch. Pharm. Chem.,* 21,449 (1914).

[2] **Evans and Diepenhorst,** THIS JOURNAL, 48,715 (1926).

aliphatic and saturated cyclic compounds, but not from ethylmagnesium bromide. On the other hand, we find Lifschitz,[3] Lifschitz and Kalberer,[4] Dufford, Calvert and Nightingale,[5] and Dufford, Nightingale and Gaddum[6] reporting no light from saturated compounds, even after repeated trials.

It now appears that the reason for these discordant observations probably lies in the effect of concentration. The writer and his colleagues had found that phenylmagnesium bromide was brightest at a concentration of about 2.5 moles to the liter of solvent, and that most of the bright compounds were best at similarly high concentrations; hence solutions less concentrated than 1 M were rarely used. However, incidental to other work carried out the past summer at the Research Laboratories, the writer found that certain aliphatic compounds, like propyl- and butylmagnesium bromides, which gave no light at concentrations as high as 1 M, gave a very faint light at reduced concentrations, the optimum concentration being about $^1/_8$ M.

These results were checked and extended for the writer by Dr. E. Q. Adams and Mr. E. R. H. Charpentier, of the Laboratories, and further extended by the writer and his colleague, Miss Dorothy Nightingale, at the University of Missouri. The results are summarized in the following statements. The aliphatic compounds butyl-, propyl-, ethyl-, and even methylmagnesium bromides, all gave faint light on oxidation; none, however, at concentrations as high as 1 M, but best at about 1/* M. In all cases the light is exceedingly faint, too weak for accurate measurement; the brightnesses were estimated to be of the order of 10^{-8} lamberts, and were very little above the threshold of visibility. Methylmagnesium iodide was doubtful, but was twice suspected of giving a momentary glow at $^1/_{64}$ M. Ethylmagnesium iodide was also exceedingly faint, but best at $^1/_4$ M. A similar effect, but with the optimum at lower concentrations, in the luminescence accompanying the oxidation of pyrogallol, has been described by E. N. Harvey.[7] The Grignard compound from trimethylene bromide gave a little more light than the compounds named above; that from bromocyclohexane gave still more, and at higher concentrations; the latter and benzylmagnesium bromide, next brightest, have their optimum concentrations above $^1/_2$ M.

These results, therefore, disprove the idea, formerly held by the writer, that it is necessary for the magnesium to be attached directly to an unsaturated carbon atom in order to obtain luminescence in ether solution; though it is still true that this condition is satisfied in all the cases where

[3] Lifschitz, Helv. *Chim. Acta,* 1,482 (1918).

[4] Lifschitz and Kalberer, *Z. physik. Chem.,* 102,393 (1922).

[5] Dufford, Calvert and Nightingale, THIS JOURNAL, 45, 2058 (1923).

[6] Dufford, Nightingale and Gaddum, *ibid.,* 49, 1858 (1927).

Harvey, *J. Biol.* Chem., *31,* 325 (1917), Table 3.

any great amount of light is obtained. Nor is the hypothesis advanced by other workers[1,2] borne out that the brightness is proportional to the molecular weight, C_2H_5MgI being fainter than C_2H_5MgBr, but the latter probably little if any fainter than C_3H_7MgBr, or brighter than CH_3MgBr. In connection with this latter idea, the writer is indebted to Dr. N. J. Beaber, of the Mellon Institute, for the suggestion, with strong evidence, that the compound formerly[5,6] regarded as p-IC_6H_4MgBr should be assigned the structure p-BrC_6H_4MgI. If this be correct, the compound should have been placed in the series p-ClC_6H_4MgI, p-BrC_6H_4MgI, p-IC_6H_4MgI, instead of the series previously suggested by the writer; but, in either case, the series would be one in which the brightness would decrease with increase in molecular weight.

COLUMBIA, MISSOURI R. T. DUFFORD

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NEW BOOKS

Handbuch der Anorganischen Chemie. (Handbook of Inorganic Chemistry.) By DR. R. ABEGG, DR. FR. AUERBACH AND DR. I. KOPPEL. Fourth Volume, Third Section, First Part. The Noble Gases. By DR. EUGEN RABINOWITSCH. S. Hirzel, Königstrasse 2, Leipzig, 1928. xii + 522 pp. 50 figs. 17 × 24 cm. Price, unbound, M. 45; bound, M. 48.

This volume represents the first instalment of the last subdivision of the Abegg Handbook. The elements which it discusses, although they exhibit scarcely any chemical activity, have nevertheless exerted a profound influence on our views as to the relationship of the elements and the structure of matter.

One can hardly escape a comparison of this volume with the corresponding one of the Gmelin Handbook recently published. Both are excellent, but the methods of presentation are radically different. This volume arranges the material under general headings, such as Occurrence of the Rare Gases; Preparation of the Rare Gases; Detection of the Rare Gases; Nuclear Properties of the Rare Gases; Atomic Properties of the Rare Gases, etc. The corresponding volume of the Gmelin Handbook, except for an introductory chapter, arranges the material wholly under each separate element. This latter method may perhaps make possible the more rapid location of the particular information desired, an advantage that is consonant with the general purposes of the Gmelin Handbook. The arrangement of the present volume, however, makes the subject matter more interesting and readable. This effect is still further favored by the inclusion of much more explanatory material and discussion of theoretical considerations. Apparently, also, a fuller presentation of the available numerical data has been attempted. Finally, it should be particularly mentioned that there is an excellent treatment of the spectra of the rare gases, from the point of view of the quantum theory.

This volume is, therefore, a valuable accession to the literature of the rare gases.

ARTHUR B. LAMB

Adsorption und Kapillarkondensation. (Adsorption and Capillary Condensation.) Band 7 of Kolloidforschung in Einzeldarstellungen. By Erich Hiickel. Akademische Verlagsgesellschaft m. b. H., Markgrafenstr. 4, Leipzig C 1, Germany, 1928. vii + 308 pp. 34 figs. 15 × 22 cm. Price, unbound, M 18; bound M 20.

A systematic treatment of the theory of the subject. The first chapter contains definitions and a very careful analysis of the thermodynamics involved. The theory is then developed, partly by thermodynamical and partly by statistical methods, beginning with the simplest possible case, adsorption on a plane surface of a number of molecules so small that their mutual influence vanishes. Attention is then paid to the complications caused by the unevenness and inhomogeneity of the surface of a real adsorbent, as well as by the mutual influences which appear when the number of molecules adsorbed increases. The final chapter is devoted to phenomena near saturation, which are considered to be caused by capillary condensation. This section is logically preceded by a review of the theory of surface tension and wetting.

The point of view from which the book is written is that of the mathematical physicist. Much emphasis is placed upon the electrical theory of the origin of adsorption forces, as developed by Debye and Jaquet. The treatment of mutual molecular influences, and of surface tension, follows van der Waals. The author is, however, by no means one-sided, but gives due consideration to other important theories of adsorption.

The book will prove a valuable stimulus to those interested in the theoretical aspects of the subject. A possible fault is the paucity of experimental illustrative material. Recent American work seems to have been overlooked.

ALBERT SPRAGUE COOLIDGE

The Mechanism of Homogeneous Organic Reactions from the Physical-Chemical Standpoint. By FRANCIS OWEN RICE, Associate Professor of Chemistry in the Johns Hopkins University. American Chemical Society Monograph Series. The Chemical Catalog Company, Inc., 419 Fourth Avenue, at 29th Street, New York, 1928. 217 pp. 11 figs. 15.5 × 23.5 cm. Price, $5.00.

The author's point of view is illustrated by a statement taken from the two-page discussion of homogeneous gas reactions with which the book concludes: "In the last year or two several homogeneous reactions in the gas phase have been studied. Although the actual examples are not catalytic it is obvious that such studies will throw much light on the mechanism of reaction kinetics and should therefore be included in any discussion of homogeneous reactions." As might be expected from this quotation, the main portion of the book is devoted to a discussion of homogeneous *catalysis,* although heterogeneous reactions are not entirely excluded. It is stated in the introduction that the intention is to give a systematic account of organic reactions from the point of view that they are all catalyzed either by dry (unhydrated) hydrogen ions or by dry hydroxyl ions. This treatment tends to unify a great amount of rather heterogeneous information, but it seems to the reviewer that some of the explanations are rather unsatisfactory; for example (p. 28), the catalytic action of hydrogen ion in the bromination of acetone is supposed to be the production of the enol form of acetone from the keto form, which is strange since the equilibrium should be shifted toward the enol form by alkali. The theory of dry-ion catalysis is successful in explaining many of the facts, including some very peculiar effects of traces of water, but in its present form at least it does not seem to be universally applicable. It would be very strange if at least one class of reactions, thermal decompositions, did not have a natural rate in the absence of all catalysts.

After a brief introductory chapter, there follows a mathematical treatment of reaction rates, devoted to the calculation of the rates from experimental data; in addition to the usual equations for first and second order reactions, a brief treatment is given of catalysis, opposing reactions, consecutive reactions and side reactions.

Chapter III is devoted to the formation of addition compounds. The results of freezing-point measurements are correlated with chemical character. This chapter will be of interest to many physical chemists who may never have considered the subject from this point of view. The statement (p. 49) that hydrochloric acid has a dissociation constant of 1.0 is unfortunate.

Chapter IV deals with various theories of reaction rates. It is, in the reviewer's judgment, the least satisfactory part of the book. The original Arrhenius postulate of activated states which are unstable tautomeric forms is outlined, and four pages are devoted to a rather vague discussion of the radiation hypothesis; there is only a brief mention of activation by collision, which has been for several years the most satisfactory way of accounting for bimolecular reactions at least, and which now seems superior to the radiation hypothesis for unimolecular reactions. The very significant theoretical papers of Hinshelwood and of Fowler and Rideal, which appeared in 1926, are not mentioned, although later experimental work of Hinshelwood is referred to.

The remaining six chapters are devoted to a consideration of various organic reactions. It is in this field that the author's own work has been done, and here his presentation is most successful. Isomeric changes, chiefly between keto and enol forms, are treated at length. Another chapter is devoted to hydrolytic reactions; this includes a brief discussion of esterification and lactone formation. Chapter VII treats the reactions of aliphatic hydrocarbons. Chapter VIII deals with substitution in the benzene ring, with emphasis on the modern work, such as the competition experiments of Francis. In place of the usual rather hackneyed restatements of Crum Brown's rule, there are quantitative statements of definite value. It is an unusually clear presentation of a very complex field. A number of other reactions, such as the Friedel and Crafts reaction and the Walden inversion, are treated more briefly in the last two chapters. The amount of material which has been compressed into these six chapters is tremendous. There is at times a tendency to become encyclopedic, but on the whole the treatment is very readable. Anyone looking for research problems in physico-organic chemistry will find the book most suggestive. There are about five hundred references to the literature, which will prove of great value to all workers in this field.

LOUIS S. KASSEL

Fortschritte der Mikrochemie in ihren verschiedenen Anwendungsgebieten. (The Progress of Microchemistry in its Various Fields of Application.) By Dr. GUSTAV KLEIN, Professor at the Biochemical Institute of the University of Vienna, and Dr. ROBERT STREBINGER, Lecturer at the Institute of Analytical Chemistry of the Technical High School of Vienna. Franz Deuticke, Leipzig and Vienna, 1928. 436 pp. 16 × 24 cm. Price, M. 24; bound, 26.6; s. 36; bound, 39.90.

The rapid growth of microchemistry during the past decade is well illustrated by the wealth of material presented in this book. The titles of the chief subdivisions will serve to indicate the method of treatment. They are as follows: Quantitative Inorganic Microanalysis; Quantitative Organic Microanalysis; Microcrystalloscopy; The Microchemistry of Minerals; Colloid Chemistry and its Relation to Microchemical Analysis; The Chemistry of Plant Tissues; The Chemistry of Animal Tissues, The Application of Microchemical Methods to the Investigation of Drugs and Poisons; and, finally, The Progress of Microchemistry from 1915 to 1926, to which the remaining 300 bdd pages are devoted.

The book presents a very adequate review of the German literature of microchemistry and allied fields, but would have a wider degree of usefulness if it covered the similar fields of literature in English more adequately. Amplification of the material dealing with the microscopy of ore minerals would enhance the value of the book to a number of investigators and the addition of a section on the application of microchemistry to sedimentary petrography would be advantageous in view of the increasing importance of the latter to petroleum geology. It is to be hoped that future editions will include an author and a subject index.

These however are rather minor points. "Fortschritte der Mikrochemie" is a serious, systematic attempt to correlate the literature of a very rapidly growing and important phase of chemistry and as such it deserves unqualified support.

LAWRENCE T. FAIRHALL

Die Alkaloide, eine Monographie der natürlichen Basen. (The Alkaloids, a Monograph on the Natural Bases.) **By Dr. GEORG TRIER, Lecturer at the Technical High School of Zürich. Second, revised edition, Part I.** Gebrüder **Borntraeger,** Schöneberger ufer 12 a, Berlin W 35, Germany, 1927. 356 **pp. 18** X **26.5 cm. Price 18** M.

This work is the first section of what is without doubt a pretentious and well-balanced treatment on the subject of the Natural Bases. The absence of a Table of Contents and an Index are to be regretted but no doubt the latter will be supplied subsequently.

This monograph will make a splendid addition to the chemist's library shelf, and may well be placed alongside Henry's "Alkaloids" and Barger's "The Simpler Natural Bases." It is less valuable and convenient to use as a reference book than either of these volumes but it differs from them in its exhaustive treatment of the historical phases of alkaloid chemistry. Its extensive discussion of the pharmacological behavior of the products is also valuable. Many references are given in these sections.

An interesting introductory chapter of thirty-four pages which abounds in historical details is followed by sections on (1) Aliphatic Bases, (2) Aromatic Bases, (3) Acid Amides, (4) Urea Derivatives (including cylic ureas such as imidazoles, purines, etc.), and (5) Heterocyclic Bases of the Pyrrole-Pyridine Group.

Serious errors are few and the more striking ones, such as the incorrect formula for novocaine (p. 55) and the assignment of the caffeine formula to theophyllin (p. 222), will be apparent to the reader. It is unfortunate that important advances made during 1926–1927 as, for example, the new information concerning Spermine, Thyroxin, Ergothioneine, etc., fail to receive attention.

The general impression gained from reading this monograph is most excellent. One is tempted to read on and on, to be sure not with the excitement created by a romance but rather with the sustained interest of a well-written biography. The reviewer called to mind his experience one summer, when he included volume one of Boswell's Life of Johnson in his vacation equipment expecting to read a few chapters only. Soon he found himself at the end of the volume, but in the woods a hundred miles from a library where the remaining five volumes might be procured. He will look forward with just as much interest to the remainder of this monograph on alkaloids.

OLIVER KAMM